The Decomposition of Hydrocarbons and The Influence of Hydrogen in Carbureted Water Gas Manufacture

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE
COLUMBIA UNIVERSITY IN THE
CITY OF NEW YORK

BY

Eugene Hendricks Leslie, B.S.

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THE DECOMPOSITION OF HYDROCARBONS AND THE INFLUENCE OF HYDROGEN IN CARBURETED WATER GAS MANUFACTURE

I—HISTORICAL REVIEW

The task of reviewing and assembling the large amount of material which has been written on the reactions of the hydrocarbons under the influence of heat is in no sense an easy one. On account of the variety of the materials which have been worked upon, the extreme complexity of the changes which take place in any case, the differences in the types of apparatus used, and the apparent inclination of many writers to allow the reader to do the greater part of the interpretation of the results, which in many cases is well nigh impossible, the presentation of this material in condensed form is accompanied by readily appreciated difficulties. Such a summary must necessarily confine itself to the work of those who seem to have added most to the knowledge in this field.

In the discussion which follows the topics taken up will be:

I—The work relative to the primary decomposition of high molecular weight paraffin and naphthene hydrocarbons.

II—The various ideas in regard to the mode of reaction of the products of the primary decomposition.

III—The pyrogenic reactions of the simpler compounds such as methane, ethane, ethylene, and similar hydrocarbons.

IV—Aromatic hydrocarbons.

V—The influence of hydrogen on these reactions.

VI—The transfer of heat in gas machines.

VII—Our own experiments.

I—PRIMARY DECOMPOSITION

It is evident that when a high molecular weight paraffin splits up into two simpler molecules both of these cannot be saturated hydrocarbons. An olefin and a paraffin result.

It might be thought that two olefins and hydrogen

could be formed. If this were the case the decomposition of pentane would be represented:

$$C_5H_{12} \rightleftharpoons C_2H_4 + C_3H_6 + H_2$$

If this were the manner of the decomposition the gases arising should contain at least 33 per cent of hydrogen whereas we know that low temperature gases contain very little hydrogen.

The other possibility that two paraffins might result with simultaneous separation of carbon is also not the case as can be seen from the analysis of low temperature oil gases shown graphically elsewhere in this paper, and also from the fact that low temperature oil cracking produces only very small amounts of carbon. That such a change is possible at low temperatures, however, in a hydrocarbon system of this sort can be seen from the fact that McAfee[1] in the aluminum chloride catalytic process obtained low boiling saturated hydrocarbons with none of the unsaturated hydrocarbons. The carbon separated out in the form of a granular coky mass. Even when the starting material was unsaturated the final products were saturated hydrocarbons and carbon. That the course of the reaction in the presence of aluminum chloride is different from that of the thermal decomposition at low temperatures is obvious.

That the primary decomposition is actually a breaking down to paraffin and olefin has been well established by the work of investigators which will be cited below, and is borne out by our own experiments which will be discussed later.

The next question which naturally arises is where does the long paraffin chain split, in the middle or near the end? And if the rupture is near the end which is the product of low molecular weight, the olefin or the paraffin? In the discussion of these questions the work of several investigators will be cited.

Vohl[2] believed that the higher paraffins decomposed primarily into a paraffin of high molecular weight and an olefin with few carbon atoms. His views, however, have not been accepted and are not in accordance with the greater portion of the experimental evidence recorded in the literature.

Thorpe and Young[3] heated solid paraffins in sealed tubes, and found that under the combined influence

[1] *J. Ind. Eng. Chem.*, **7** (1915), 737–741; *Met. Chem. Eng.*, **13** (1915), 592–597.

[2] *Dingler's polytech. J.*, **177**, 69.

[3] *Proc. Roy. Soc.*, **21**, 184–201.

of heat and pressure a mixture of olefins and paraffins of lower boiling point was obtained. They believed this mode of decomposition to be general, but were unable to bring forward experimental evidence as to whether the change gave rise to an olefin of low molecular weight with a larger paraffin residue, or *vice versa*.

Prunier[1] found that butylene, propylene, ethylene, and some crotonylene were formed when light petroleum vapors were passed through a glowing tube.

H. E. Armstrong[2] reported the finding of considerable quantities of amylene and hexylene along with aromatic hydrocarbons in the compression liquids from Pintsch gas manufacture. Paraffins were not present. A gaseous compound was dissolved in these liquids which gave a bromide of the formula $C_4H_6Br_4$, and which, according to Armstrong, was probably methylallene, $CH_3—CH=C=CH_2$.

Brochet[3] identified normal butylene, normal amylene, normal hexylene, and piperylene in the compression liquids from Pintsch gas manufacture.

Lewes[4] found hexylene and heptylene in the tar obtained by the cracking of Russian oil.

Brooks[5] examined a compression liquid from the Pintsch gas process and found it to contain 48.0 per cent of unsaturated products removable by cold concentrated sulfuric acid. The rest was chiefly benzene. Experiments carried out by him showed that solar oil when treated at temperatures between 430° C. and 600° C. yielded 3 to 20 per cent of gasoline boiling below 150° C. This product was highly unsaturated. Treatment with cold concentrated sulfuric acid caused a 20 per cent loss. When nickel was used along with the oil more gas was produced and the product contained more unsaturated hydrocarbons.

Armstrong and Miller[6] examined the liquid products which resulted when oil gas was compressed, and found that it contained considerable quantities of amylene and its next two higher homologs, but not the corresponding paraffins. This apparently is evidence in favor of the view that the initial decomposition of the oil is such as to give rise to a high molecular weight olefin and a low molecular with paraffin;

[1] *Ber.*, **6** (1873), 72.
[2] *J. Soc. Chem. Ind.*, **3** (1884), 462–468.
[3] *Compt. rend.*, **114** (1892), 60.
[4] *J. Soc. Chem. Ind.*, **11** (1892), 584, *et seq.*
[5] *J. Frank. Inst.*, **180** (1915), 653–673.
[6] *J. Chem. Soc.*, **49** (1886), 74–93.

for if paraffin and olefin of nearly the same molecular weight had been formed we should expect that a preponderance of paraffins would have been found in the liquid resulting from the compression. It is well known that the paraffins with carbon chains of three atoms or over are more stable with respect to the influence of heat than the corresponding olefins.

Norton and Andrews[1] passed vapors of hexane and pentane through glass or porcelain tubes 15 mm. in diameter and 70 cm. long heated to a bright red heat. In their experiments on hexane a liquid collected in the receiver which was approximately 10 per cent by weight of the hexane used, and which contained unchanged hexane, hexylene, amylene, and a little benzene. The hexylene and amylene were not present in large amount, but this would not be expected when the temperature of their experiments is taken into consideration. They found large amounts of propylene and ethylene which they collected by passing the gases through bromine, and these hydrocarbons no doubt arose from the secondary decomposition of amylene.

J. F. Tocher[2] destructively distilled octane and decane. He says in the discussion of his results that they "bear out that at low temperatures octane and decane are decomposed into ethylene and higher olefins, methane, and hydrogen, while at higher temperatures no higher olefins are formed, the gaseous products being simply ethylene, methane, and hydrogen." Thus again emphasis is laid on the presence of higher olefins without the corresponding paraffins.

Haber[3] studied the decomposition of normal hexane believing that its mode of decomposition was similar to that of the still higher paraffins. He vaporized the hydrocarbons and passed the vapors through a tube $^1/_8$ in. in diameter and 25 in. long heated to temperatures at intervals between 448° and 800° C. The low temperature was used to avoid the secondary decomposition which plays so important a part at higher temperatures. The hexane was not appreciably decomposed at 518° C. At 600° to 700° C. the gaseous products contained slightly over 50 per cent olefins, 34 to 37 per cent saturated hydrocarbons (of which approximately 70 per cent was methane) and 10 to

[1] *Am. Chem. J.*, **8** (1886), 1–9.

[2] *J. Soc. Chem. Ind.*, **13**, 231–237.

[3] *J. Gasbel*, **39** (1896), 377–382, 395–399, 435–439, 452–455, 799–805, 813–818, 830–834; *Ber.*, **29** (1896), 2691–2700.

13 per cent hydrogen. From a number of such experiments Haber concluded that the primary decomposition took place largely in accordance with the equation $C_6H_{14} \rightleftarrows C_5H_{10} + CH_4$, and from the relations between the amounts of gaseous and liquid olefins, and the mean molecular weight of the olefins in the gaseous state he was led to believe that a portion of the amylene decomposed into propylene and ethylene thus: $C_5H_{10} \rightleftarrows C_3H_6 + C_2H_4$. In any case Haber was convinced that the primary decomposition of the higher fatty hydrocarbons involved the splitting off of hydrocarbons of less than three carbon atoms with the formation of practically no hydrogen. The higher the temperature the greater the tendency for the splitting off to take place near the end of the chain.

Kramer and Spillker[1] distilled a heavy hydrocarbon oil at 450° C. and under 20 atmospheres pressure. Considerable gas was formed which contained 20 per cent olefins and 80 per cent methane. The liquid distillates contained large amounts of olefins. These observations are in accordance with the view that the chief initial reaction is a splitting into high molecular weight olefins and low molecular weight paraffins.

Engler[2] believes that the decomposition of high molecular weight paraffins begins at 200 to 250° C. at ordinary pressure. Still residues which he has examined were composed largely of olefins and their polymerization products. In his study of the cracking of a heavy Galician oil residue he found that the amount of olefins in the cracked distillate was highest in the high boiling fractions, and that the higher the cracking temperature the higher the per cent of olefins. It should be remembered that the temperatures used were never high, for the liquid phase was always present. In "Das Erdöl," page 567, Engler expresses the belief that at ordinary pressure the effect of heating is to split off low molecular weight hydrocarbons from the end of the chain, while with heating under pressure the tendency is for the long chain to split in the middle. That there might be some such difference can be seen from a consideration of the application of Le Chatelier's principle to this case.

Worstall and Burwell[3] in a study of the hydrocar-

[1] *Ber.*, **33** (1910), 2205.
[2] "Das Erdöl," p. 566.
[3] *Am. Chem. J.*, **19** (1897), 815–845.

bons of the tars from the decomposition of heptane and octane in Pintsch gas retorts found that though the tars contained unchanged heptane and octane, they contained none of the lower paraffins. Unsaturated compounds composed a third of the tars. These observations appear as an excellent corroboration of the idea that the primary decomposition is in large part a splitting off of a low molecular weight paraffin such as methane. Otherwise propane, butane, pentane, and hexane should have been found in these tars, for these hydrocarbons are more stable under the influence of heat than the corresponding olefins or the original heptane and octane.

Hempel[1] passed oil vapors through an iron tube at temperatures below 700° to 800° C. and concluded from a consideration of his gas analyses that the groups splitting off were chiefly those of one or two carbon atoms. The decomposition into methane and higher molecular weight olefins must predominate because of the high content of methane in the gases obtained. Hempel's views are essentially in accord with Haber's.

Hall[2] brought out well the dependence of the mode of primary decomposition of a long chain paraffin hydrocarbon on the temperature and pressure. He found that increase of pressure greatly diminished the yield of fixed gases, *i. e.*, methane, etc. Temperature was of great importance. At 560° C. a change of 20° made a difference of 50 per cent in the gas production, and a difference in the gravity of the liquid boiling below a certain point, the greatest difference being in the unsaturated portion. A 40° C. temperature change made as much as 40 per cent difference in the unsaturated portion. Distillates containing from 30 per cent to 90 per cent unsaturated hydrocarbons can be produced by changing no other condition than the temperature. These facts mean that the hydrocarbon chain can break at any point. The reactions which actually take place depend on the conditions. It is natural to suppose that increase of pressure would tend to give precedence to those reactions whose products occupy the least volume, *i. e.*, a splitting near the middle of the chain giving liquid products. The large increase in the percentage of olefins in the liquid products with rise of temperature indicates that the higher temperatures favor decomposition near the end of the chain, for otherwise the paraffins which are more

[1] *J. Gasbel*, **53** (1910), 53–58, 77–83, 101–105, 137–141, 155–165.
[2] *Gas World*, **62** (1915), 187, *et seq.*

stable than the corresponding olefins would predominate in the liquid products.

Ipatiew and Dowgelewitsch[1] found that hexane was decomposed at 710° C. yielding 40 to 50 per cent hydrocarbons of the C_nH_{2n} series, 8 to 14 per cent hydrogen, and 40 per cent paraffins. Hexamethylene heated for some time at 500 to 510° C. and under 70 atmospheres pressure gave a quantity of gas which was largely methane and hydrogen. The liquid products contained considerable amounts of olefins, and also methyl cyclopentane.

It seems that the mode of the pyrogenic decomposition of the naphthenes is not so different from that of the paraffins, with a few added complications such as rearrangement to the more stable five-carbon ring and dehydrogenation to aromatics.

Burgess and Wheeler[2] found a considerable evolution of higher olefins from coal up to 350° C. They believed that these hydrocarbons arose from the decomposition of a paraffin or other similar long chain hydrocarbon.

Brooks, Bacon, Padgett, and Humphrey,[3] in discussing the cracking of higher hydrocarbons, pointed out that the fatal difficulty with all processes attempting to produce gasoline from the higher hydrocarbons was the large percentage of olefins contained in the product. According to these authors this figure will vary from 20–50 per cent, depending on the temperature at which the oil is cracked. An interesting observation which bears on the mechanism of the primary decomposition was that the gases evolved during the distillation of paraffin under 100 lbs. pressure at temperatures between 350° and 450° C. consisted of 75–62 per cent saturated hydrocarbons, 25 to 37 per cent olefins, with 0.0 to 3 per cent hydrogen. The saturated hydrocarbons were not examined, but as only the lower paraffins are gaseous, and as it is common experience that, where the gaseous paraffins are formed at all, methane always predominates it is not unfair to assume that a large proportion of the gases obtained here was methane.

Pressure would be unfavorable to such a reaction as

$$C_nH_{2n+2} \longrightarrow C_{n-1}H_{2n-2} + CH_4.$$

Nevertheless such reactions constitute the most im-

[1] *Ber.*, **44** (1911), 2987–2992.
[2] *J. Chem. Soc.*, **105** (1914), 131–140.
[3] *J. Ind. Eng. Chem.*, **7** (1915), 180–185.

portant chemical change taking place when these higher hydrocarbons are heated even at 100 lbs. pressure and only 450° C. The conclusion then must be that the change in concentration on account of increased pressure has a more important effect than the shifting of the equilibrium point of the reaction.

The most exact work on the separation of the individual hydrocarbons resulting from the decomposition of the hydrocarbons of high molecular weight is that of Burrell, Seibert, and Robertson.[1] By a series of careful fractionations at low temperatures these investigators have determined the percentages of the various components in Pittsburgh coal gas and water gas. The following table shows their results:

Component	Coal Gas	Carbureted Water Gas
Carbon dioxide	1.4	4.8
Oxygen	0.7	(*a*)
Carbon monoxide	7.9	29.8
Hydrogen	50.6	32.0
Methane	31.1	13.1
Ethane	0.9	2.9
Ethylene	2.1	9.8
Propylene	0.3	2.8
Butylene	0.1	1.7
Butane	...	...
Propane	...	0.3
Benzene(*b*)	1.4	1.5
Nitrogen	3.5	1.3
Total	100.0 per cent	100.0 per cent

(*a*) Results calculated to air-free basis.
(*b*) Benzene or vapor having an inappreciable pressure at —78° C.

The notable feature of these results, so far as their bearing on the primary decomposition of hydrocarbons is concerned, lies in the fact that the percentages of olefins were always higher than the percentages of paraffins of the same number of carbon atoms. Thus in water gas there was 2.8 per cent propylene, but only 0.3 per cent propane and 1.7 per cent butylene, but only traces of butane. When the relative stability of these hydrocarbons is kept in mind, and also the temperatures at which these gases were made, these results appear as good evidence that under water gas carbureter and superheater conditions the splitting off of low molecular weight paraffins with formation of high molecular weight olefins is the chief primary reaction.

Egloff and Twomey[2] have cracked a gas oil derived from Pennsylvania crude petroleum at atmospheric pressure, and at temperature intervals of 50° C. between 450° C. and 800° C. In the cracked oils it was found that the per cent of unsaturated com-

[1] U. S. Bur. of Mines, *Tech. Paper*, **104**.
[2] *Met. Chem. Eng.*, **14** (1916), 247–250.

pounds increased with the temperature. In the distillation cut to 150° C. the per cent of unsaturateds reached a maximum of 44 per cent at 550° C. and decreased to practically 0 per cent at 800° C. The fractionation of the cracked oils was made in six cuts: 95° to 120° C., 120° to 150°, 170° to 230°, 230° to 270°, and 270° to tar. In the first of these cuts it was found that the percentage of unsaturateds reached a maximum at 550° to 600° C. while in the latter three cuts there was a steady increase with temperature in the proportion of unsaturateds. The authors believed that the decrease in olefin formation might be accounted for by polymerization of olefins to naphthenes which in turn go to aromatics, and secondly direct polymerization of olefins to aromatics. Another factor, no doubt, contributes in large degree to the observed diminution in the per cent of olefins in the low boiling cuts with increase in temperature, namely decomposition of the olefins to gaseous products of lower molecular weight. This is discussed more at length elsewhere in this paper.

The results of Egloff and Twomey are just those which would be expected if it is considered that at low temperatures the tendency of the higher molecular weight paraffins is to split into paraffin and olefin of nearly equal chain, while at higher temperatures the primary decomposition is into high molecular weight olefin and low molecular weight paraffin.

II—SECONDARY DECOMPOSITION OF HYDROCARBONS

Two classes of secondary reactions must be taken into account, *first* those which result in the breaking down of the hydrocarbon molecules to hydrocarbons of lower molecular weight, and *second* those synthetic reactions which give rise to more complex but more stable hydrocarbons.

In reviewing the work bearing on the primary decomposition of paraffin hydrocarbons of high molecular weight it has been shown that the greater portion of the experimental evidence points to a splitting of the carbon chain with formation of olefin and paraffin, and that conditions determine where the rupture takes place—low temperature and high pressure tending to favor the splitting near the middle of the chain while at lower pressures and higher temperatures the breaking off of low molecular weight hydrocarbons, such as methane, ethane, and ethylene, but particularly methane and ethane, becomes the important reaction.

The members of the paraffin series down to butane in all probability follow some such mode of reaction as this. The first problem to be considered in the study of the secondary reactions, then, is the fate of the high molecular weight olefins which arise.

If, for the sake of simplicity, pentylene, CH_2CH_2-$CH_2CH{=}CH_2$, be regarded as typical of the higher olefines we may list a few of the possible reactions as follows:

(1) $CH_3CH_2CH_2CH{=}CH_2 \rightleftharpoons CH_3CH{=}CH_2 + CH_2{=}CH_2$

(2) $CH_3CH_2CH_2CH{=}CH_2 \rightleftharpoons CH_4 + CH_3{-}C{\equiv}C{-}CH_3$

(3) $CH_3CH_2CH_2CH{=}CH_2 \rightleftharpoons CH_2\langle CH_2{-}CH_2 \rangle$

(4) $CH_3CH_2CH_2CH{=}CH_2 + H_2 \rightleftharpoons CH_3CH_2CH_2CH_2CH_3$

(5) Condensation

It is not to be imagined that any one of these reactions is the sole reaction, nor is this to be regarded as in any sense a complete list of the possible concurrent reactions. The extent to which any or all of these changes take p'ace is dependent on the temperature, pressure and concentrations. It is in an effort to discuss the extent to which each comes into play, and the effect of varying conditions that the work is reviewed bearing on this phase of the subject and that later our own experiments are considered.

Engler and Routala[1] heated 350 g. of amylene in sealed glass tubes at 325° C. for 32 days. About ten liters of gas were produced of which over 90 per cent was paraffin, 7.5 per cent hydrogen, and the rest olefins. The liquid product contained a great variety of hydrocarbons of the paraffin and polymethylene series. Also the higher boiling portions contained compounds of lower hydrogen content than the cycloparaffins.

The presence of the gaseous paraffin compounds and the high boiling compounds with more than one double bond can be explained if it is assumed that the amylene splits into methane and divinyl, $CH_2{=}CH{-}CH{=}CH_2$, or into methane and crotonylene, reactions analogous to (2) above.

$$\begin{matrix} CH_3 \\ \quad\diagdown \\ \quad\quad C{=}CH{-}CH_3 \\ \quad\diagup \\ CH_3 \end{matrix} \rightleftharpoons CH_4 + CH_3{-}C{\equiv}C{-}CH_3$$

Crotonylene

[1] *Ber.*, **42** (1909), 4620–31.

The divinyl, or crotonylene, under the influence of heat and pressure, might easily polymerize to high molecular weight compounds of low hydrogen content.

The naphthenic compounds in all probability resulted from the polymerization of the decomposition products of amylene, such as ethylene and propylene or the substituted ethylenes and propylenes; or by a rearrangement of the amylene molecule as in reaction (3).

Engler[1] stated that long chain olefins split easily into ethylene. The importance of reactions resulting in higher molecular weight hydrocarbons of lower hydrogen content was emphasized. Naphthenes were found in the product from the heating of still residues at 300° C., and since these compounds were not present in the still residues originally, Engler concluded that they were formed by polymerization of ethylenes. He was of the opinion that direct closing of the olefin chain did not take place, but this was not proved by experimental evidence.

Worstall and Burwell[2] have worked on oil gas tars in an effort to determine whether or not naphthenes were present. They mentioned that the absence of naphthenes in residues from nitration or sulfonation is not evidence that there were no naphthenes in the original tar, for the naphthenes nitrate to nitrohydrobenzenes. Such compounds have been obtained by the use of dilute nitric acid.[3] From distillation methods and specific gravity tests the authors concluded that their oil gas tars contained no naphthenes.

It is to be kept in mind here that oil gas in the Pintsch gas process is made at temperatures of 850° to 900° C., and it is probable that this accounts for the difference between the results of these authors and those of Engler whose work was carried out at lower temperatures; *i. e.*, between 300° and 400° C.

Haber,[4] on the other hand, was convinced by a study of the combustion data of oil gases made from hexane at temperatures of 600° C. and above that naphthenes were present. He also believed that crotonylene was formed in small amounts by the splitting off of methane from amylene. Emphasis was laid on the synthetic reactions such as the building up of high molecular

[1] *Ber.*, **30** (1897), 2908.

[2] *Am. Chem. J.*, **19** (1897), 815–845.

[3] *Ber.*, **25** (1892), 107–108; **28** (1895), 577–578.

[4] *J. Gasbel*, **39** (1896), 377–382, 395–399, 435–439, 452–455, 799–805, 813–818, 830–834.

weight compounds by the combination of "free unsaturated residues."

H. E. Armstrong[1] found a gas dissolved in the compression liquids from oil gas manufacture which gave a bromide of the composition $C_4H_6Br_4$, and which he believed to be methylallene, $CH_3—CH=C=CH_2$.

Armstrong and Miller,[2] in the examination of similar liquids, found olefins of the type C_nH_{2n-2}. Vinyl ethylene, $CH_2=CH—CH=CH_2$, was identified.

A. Harzer[3] commented on the fact that there was a considerable proportion of diolefins among the hydrocarbons of coal and coal tar.

Jones and Wheeler[4] made note of their observation that one-fifth by weight of the tar formed in their vacuum distillations of coal at low temperatures was composed of olefins, the greater part of which was richer in carbon than the mono-olefins. This appears an excellent evidence that the decomposition of the higher olefins into methane and diolefins or substituted acetylenes is really one of the reactions in the course of the breaking down of these long chain olefins; for the conditions used here, *i. e.*, low temperature and low pressure, are those which tend to preserve intermediate products, and not those which would be likely to give rise to diolefins through synthetic reactions.

W. A. Noyes, W. M. Blinks, and A. V. H. Morey[5] made oil gases at comparatively low temperatures in a checkerbrick filled machine. The gases were analyzed for olefins by passing them through bromine water, and subsequently fractionating the bromides formed. In this manner they found that of the 28.1 per cent olefins present 16.2 per cent was ethylene and 11.9 per cent propylene.

Norton and Andrews,[6] in their work on the pyrogenic decomposition of hexanes and pentanes, passed the gases through bromine dissolved in carbon disulfide. The liquid bromides so formed were found to be ethylene and propylene dibromides in nearly equal proportion. This observation and that of Noyes, Blinks, and Morey, is entirely in accord with the belief that reactions such as the first one mentioned in the list above take place,

[1] *J. Soc. Chem. Ind.*, **3** (1884), 462–468.
[2] *J. Chem. Soc.*, **49** (1886), 74–93.
[3] *Gas World*, **59** (1913), 405.
[4] *J. Chem. Soc.*, **105** (1914), 140–151, 2562–2565.
[5] *J. Am. Chem. Soc.*, **16** (1894), 688–697.
[6] *Am. Chem. J.*, **8** (1886), 1–9.

$$C_5H_{10} \rightleftarrows C_3H_6 + C_2H_4$$

i. e., a splitting of higher olefins into lower olefins. Norton and Andrews also found that there was formed a solid bromide of the composition $C_4H_6Br_4$, which was evidently the bromide of divinyl or crotonylene rather than ethyl acetylene, since the hydrocarbons passed through a solution of ammoniacal cuprous chloride before being led into the bromine solution. Ethyl acetylene would have formed a copper compound, and thus have been removed.

That the higher olefins are intermediate between the paraffins and the low molecular weight gaseous compounds can be seen by a study of some further work of Norton and Andrews. When hexane was passed through a 15 mm. diameter glass tube at 700° C., and the products collected it was found that a large portion of the hexane passed through unchanged. But the liquid which was collected also contained a mixture of butylene, amylene, and hexylene. The bromides obtained by passing the gases through bromine in carbon disulfide were propylene dibromide, crotonylene dibromide, but no ethylene dibromide. At higher temperatures the decomposition of isohexane gave, beside the liquid products, gaseous hydrocarbons which proved to be largely propylene and crotonylene with smaller amounts of ethylene. Similar results were obtained when pentane was pyrogenically decomposed.

The statement as to the absence of ethylene in the 700° C. gases from hexane should, as judged from general experience, be accepted with reservations. However, it must be kept in mind that 700° C. as measured and applied to a certain kind and size of apparatus may give results similar to those of very different temperatures in a different apparatus used by another observer.

Lewes[1] decomposed Russian oil in a short retort at 500° C. in order to study the early stages of the decomposition of hydrocarbons. He found the paraffins and olefins present in nearly equal proportions in the gases. Increase of temperature diminished the per cent of olefins. As the temperature went up the paraffins, too, reacted secondarily, but this was with formation of methane so that the actual percentage of paraffin in the gas did not decrease, but increased.

Hempel[2] was evidently of the opinion that the

[1] *J. Soc. Chem. Ind.*, **11** (1893), 584–590.

[2] *J. Gasbel*, **53** (1910), 53–58, 77–83, 101–105, 137–141, 155–165.

higher olefins changed rather easily into ring compounds, and pointed to the considerable quantity of these latter compounds which were contained in oil gas tars. His experimental work showed that when oils were cracked in atmospheres of hydrogen considerable hydrogen was actually absorbed, and that the yields of methane, ethane and ethylene per unit weight of oil were larger. His observations are discussed more at length elsewhere in this paper, but it should be noted here that hydrogenation of these higher olefins is not an improbable reaction.

W. Ipatiew[1] studied the polymerization of ethylene and some of its homologs. At 380° to 400° C. and 70 atmospheres pressure the polymerization of ethylene is very rapid. The lower boiling fractions of the products contained paraffins, and the higher boiling fractions olefins and polymethylenes. No benzene hydrocarbons were obtained. The higher fractions also contained some hydrocarbons of higher carbon percentages and lower hydrogen content than the C_2H_{2n} series. Isobutylene yielded products analogous to those obtained from ethylene except that the hydrocarbons richer in carbon than the mono-olefins were not present. Ipatiew believed that condensation to hexamethylene was the first step in all these reactions.

The work of Burrell, Seibert and Robertson[2] has already been referred to in our discussion of the primary decomposition of hydrocarbons. Further valuable conclusions can be drawn from it, however, which concern the changes undergone by the high molecular weight olefins. The authors found that Pittsburgh carbureted water gas contained 15.9 per cent illuminants, and Pittsburgh coal gas 3.9 per cent illuminants. The following table shows the proportions of the various components which go to make up these totals:

Component	Coal Gas	Carbureted Water Gas
Ethylene	53.8	60.9
Propylene	7.7	17.4
Butylene	2.6	10.6
Propane	....	1.8
Butane	....	....
Benzene(*a*)	35.9	9.3

(*a*) Vapors having an inappreciable pressure at —78° C.

The proportions of ethylene, propylene and butylene are notable. These results may be interpreted as indicating that reactions such as $C_5H_{10} \rightleftarrows C_3H_6 +$

[1] *Ber.*, **44** (1911), 2978–2987.

[2] U. S. Bureau of Mines, *Tech. Paper*, **104**.

C_2H_4 actually play an important part in the breaking down of the higher olefins.

No mention was made by Burrell, Seibert and Robertson of the naphthenes. The hexamethylene compounds boil from 81° C. up, and might pass largely into the water gas tar. A portion of the component marked benzene in the above table may easily have been hexamethylene. Pentamethylene, however, boils at 49° C., and if it were formed in significant amounts it should be found in the gases. Apparently, therefore, compounds of this class are not formed in large amount when the hydrocarbons undergo a decomposition under the conditions of carbureted water gas manufacture.

SUMMARY—It seems, then, that the chief reaction undergone by these high molecular weight olefins is a splitting into lower molecular weight olefins. A decomposition into methane and compounds with two double bonds or one triple bond also takes place. The intramolecular change of olefins into cycloparaffins is possible, but from the evidence available it is difficult to state what proportion of the naphthene formation must be ascribed to this reaction. Hydrogenation of olefins takes place to some extent. Polymerization of olefins to naphthenes occurs, also polymerization of the high molecular weight unsaturated compounds to tarry compounds.

III—TERTIARY DECOMPOSITION

The problem now becomes one of studying the reactions of the hydrocarbons which are formed in the primary and secondary decompositions of the paraffins. These products are ethylene, propylene, diolefins, acetylenes, naphthenes, methane, ethane, propane, and the high molecular weight tarry compounds. The discussion of the changes which these hydrocarbons undergo separately may appear fundamentally wrong in view of the fact that in the hydrocarbon system undergoing change these reactions are all interlocked and related in a most complex manner. However, it is just on account of this complexity that the manner of presentation of the material which follows has been chosen—that is a consideration of the reactions of the separate hydrocarbons. Before turning to such a discussion, however, it is desired to point out a few things in connection with such hydrocarbon systems as a whole.

The earliest attempt to elucidate in anything like

a comprehensive manner the changes taking place in a hydrocarbon system was made by Berthelot.[1] He heated hydrocarbons in a retort, and also by passing them through a tube. From rather meager data on a few of the lower molecular weight hydrocarbons a theory of thermal decomposition was worked out. Berthelot found that ethylene and hydrogen when heated in a retort gave some ethane, and that ethane formed ethylene in small quantities. Ethylene was formed from acetylene and hydrogen. Ethylene alone gave small amounts of acetylene and ethane; and liquid products of the formula of crotonylene resulted when acetylene and ethylene were heated together. When the gases were passed through the tube methane gave acetylene, olefins, ethane, naphthalene, and tar. From these experiments Berthelot concluded that two types of reactions were at work—reactions of decompositions, and synthetic reactions. The breaking down and building up changes competed with each other and a complex equilibrium was supposedly established.

Berthelot's work has been criticized by Haber on the ground that conclusions could not be drawn regarding hydrocarbon reactions in general from a study of a few of these simple hydrocarbons because they constitute a special case. For instance, ethylene cannot split open a carbon bond without completely disrupting the molecule, whereas a long chain olefin can easily break open in this fashion. Furthermore, Berthelot heated these substances in a closed retort. These conditions are obviously not those which should be chosen for a study of the mechanism of the reactions, for such heating would give only those products which stand long heating, and not those which might have been formed transitorily. Also Berthelot's equilibrium idea is criticized by Haber for the reason that it would necessitate the presence of almost every conceivable hydrocarbon, whereas, though the system is complex enough, it does not exhibit such a heterogeneous composition as this.

That Haber's criticisms of Berthelot's experimental methods and of his general conclusions are well placed can be seen from a consideration of recent work and also from the results of the experimental work recorded in this paper.

Whitaker and Alexander[2] have shown that when

[1] *Ann. chim. phys.*, **67**, iii (1863), 53; **9**, iv (1866), 413, 455; **12**, iv (1867), 5, 122; **16**, iv (1869), 143, 148, 153, 162.

[2] *J. Ind. Eng. Chem.*, **7** (1915), 484–495.

paraffin hydrocarbons are cracked at temperatures of 1400° to 1600° C. the olefins no longer exist, though the gases still contain approximately 2% of methane. If the oil rate was still further decreased the methane disappeared and carbon and hydrogen were the only products.

It is generally recognized that the most stable gaseous hydrocarbons are methane, ethane and ethylene. Ethane is formed in much smaller amount than either of the other two, hence even though it may be more stable than ethylene the latter persists longer in detectable amounts because it was originally present in larger proportion. Any hydrocarbon system heated above 700° C. will tend toward these products, and if given time these gases, along with carbon and hydrogen, will be the chief products. With the lapse of more time the ethane and ethylene decompose with formation of methane, carbon and hydrogen, which are the ultimate products. The methane equilibrium is discussed elsewhere in this paper, and it is seen that methane exists in quantity only at those temperatures below 750° to 800° C.

A gaseous hydrocarbon system is thus not really in equilibrium. Rather the condition of such a system may be compared to that of a mixture of hydrogen and oxygen gases at temperatures of 200° to 300° C. The equilibrium condition of such a system is practically a complete union forming water, but the speed of the reaction $2H_2 + O_2 \longrightarrow 2H_2O$ is so small at these temperatures that the system might easily be thought to be in equilibrium, *i. e.*, in that condition which is independent of the further passage of time.

Even though it has been established that a true condition of equilibrium does not exist there is still an interdependence of reactions in a hydrocarbon system. This idea has been elaborated by Whitaker and Rittman.[1]

The reactions which form the lower molecular weight hydrocarbons are in general more rapid in their progress than the reactions of decomposition of these lower hydrocarbons. Methane, in particular, is stable under the action of heat at those temperatures which are used in the various apparatus used in the manufacture of gas. Thus those reactions which result in the formation of methane and ethylene reach a condition nearly corresponding to equilibrium

[1] *J. Ind. Eng. Chem.*, **6** (1914), 383–392, 472–479.

proportions on account of the slow decomposition of ethylene and methane, but the system as a whole cannot be regarded as in equilibrium.

In considering the discussion of the reactions of the individual hydrocarbons the effect of the presence of the end-products of a particular reaction must always be kept in mind. Also the changing concentration conditions as the gas volume increases with the progress of the changes involved must not be forgotten.

REACTIONS OF METHANE

The study of the influence of heat at various temperatures on the hydrocarbon methane has usually been made with the idea in mind of finding the equilibrium proportions of methane and hydrogen in the system carbon–hydrogen–methane.

The equilibrium proportions are never even approximated in experiments made after the manner of those discussed in the latter part of this paper, nor under the conditions maintained in the technical production of coal, oil, and water gas. The preservation of methane is desired in all these cases, for its decomposition into carbon and hydrogen means loss of valuable carbon from the gas and the production of gases high in hydrogen which are unsuited for distribution. Hence the studies of the methane equilibrium are of interest only in so far as they indicate the tendency of methane to decompose under certain temperature conditions.

Mayer and Altmayer[1] studied the methane equilibrium between 475° and 625° C., and found that below 625° C. appreciable quantities of methane were stable. They deduced a mathematical expression by means of which they extrapolated their experimental results to 250° C. on one hand and 850° C. on the other. Finding that at 850° C. the calculated percentage of methane in equilibrium with carbon and hydrogen would be only 1.59, they stated that at temperatures as high as 1200° C. no methane could be formed synthetically. This conclusion was severely criticized by Bone and Coward[2] on the ground that the low temperature experimental range would not justify such wholesale extrapolation. This appears as a most just criticism. Bone and Coward have, in fact, converted 73 per cent of a quantity of

[1] *Ber.*, **40** (1907), 2134–2144.

[2] *J. Chem. Soc.*, **93** (1908), 1975–1993, and **97** (1910), 1219–1225.

pure carbon into methane at 1100°–1200° by passing hydrogen over it. The equilibrium proportion of methane at these temperatures is exceedingly minute, however.

Earlier work done by Bone and Jerdan[1] on the synthesis of methane at 1200° C. and above, has been criticized by Berthelot,[2] who did not believe that methane could be synthesized at such high temperature, if the reaction materials were pure. Bone and Coward's results, however, appear to show that this is not true.

Pring and Hutton[3] obtained 0.10 to 0.25 per cent methane by electrical heating of purified carbon rods in atmospheres of hydrogen at 1250° to 1350° C. They also found 0.5 to 3.6 per cent acetylene formed at temperatures between 1800° and 2500° C. The amount of acetylene increased fairly regularly with the temperature. At these same temperatures amounts of methane ranging from 0.5 to 1.0 per cent were found in the gases, being formed no doubt largely by the decomposition of the acetylene, and then moving out of the heated zone and escaping destruction.

Pring and Fairlie[4] have studied the methane equilibrium. They noted that at temperatures below 1000° C. the union of carbon and hydrogen was so slow, even with application of pressure, that the equilibrium proportions could not be reached in any reasonable length of time. Ethylene began to be formed at 1300° C., and the quantity in equilibrium at 1400° was 0.005 per cent. Acetylene was first formed at 1650° C., and the amount increased with the temperature at those temperatures. Where ethylene and acetylene are capable of formation the exact determination of the methane equilibrium is impossible because of the decomposition of these gases into methane. The amounts of methane in equilibrium are: at 1200° C., 0.20 per cent; and at 1500° C., 0.07 per cent.

T. Holgate[5] pointed out that the curve expressing the rate of decomposition of methane with rise of temperature has a maximum at about 600° C. He believed that this was due to the accumulation of hydrogen which acted as a brake to the decomposi-

[1] *J. Chem. Soc.*, **71** (1897), 41–61.
[2] *Ann. chim. phys.*, **6** viii (1905), 183.
[3] *J. Chem. Soc.*, **89** (1906), 1591–1601.
[4] *Reports 8th Internat. Congress*, **21**, 65.
[5] *J. Gas Lighting*, **106** (1909), 25–28, 84–86.

tion. Holgate evidently believed that the reaction $C + 2H_2 \longrightarrow CH_4$ had an appreciable speed, for he said that above 607° C. "the retarding action of the square of the hydrogen pressure is greater than the effect of heat in driving the reaction, and as a result there is at 800° C. a less increase in the rate of decomposition of the methane per degree rise in temperature than there is at 400° C." This explanation is not in accordance with the various investigations of the methane equilibrium which have shown that the speed of the reaction $C + 2H_2 \longrightarrow CH_4$ is inappreciable at temperatures less than 1000° C.

Ipatiew[1] has shown that even in the presence of the catalysts NiO or reduced nickel, which have proved most effective in promoting gaseous reactions, the union of carbon and hydrogen could not be detected at 650° C.

On the other hand, general experience shows that at temperatures above 600° C. the production of gases of all kinds is greatly increased, and the time of heating of the gaseous mixture is diminished in proportion to this increase in volume. This accounts for the fact that the hydrocarbons are not destroyed before leaving the coal gas retorts of the water gas superheater. In thinking of the hydrocarbon systems involved here it must be kept in mind that the reverse reactions of these breaking down reactions have small velocities, largely on account of the removal of the end-products of the decompositions by other changes.

It can be seen from the researches cited that methane is actually tending to decompose into carbon and hydrogen at the temperatures normally operative in water gas or oil gas machines or coal gas retorts. That this decomposition can actually be brought about on a large scale is well shown by the work of Ostromisslinski and Burshanadse,[2] who made a gas containing 75 to 80 per cent hydrogen and suitable for filling balloons by passing hydrocarbon gases over nickel, nickel oxide, or oxides of iron.

Brownlee and Uhlinger[3] made a gas containing 90 to 95 per cent hydrogen by passing natural gas or the vapors of liquid or solid hydrocarbons over highly heated refractory material.

More interesting from a practical or working point of view than the investigations of the methane equi-

[1] *J. prakt. Chem.*, **87** (1913), 479–487.
[2] *J. Russ. Phys.-Chem. Soc.*, **42** (1910), 195–207.
[3] U. S. Pat. 1,168,931, Jan. 18, 1916.

librium, are the results of those experiments wherein the working conditions approximate those of actual practice.

Simmersbach[1] analyzed coke oven gases which were heated over refractory materials for 10 to 14 seconds. The proportion of methane in these gases at 800° C. was 27.6 per cent, at 1000° C. 20.2, at 1100° C. 15.6, and at 1200° C. 5.5 per cent. All other hydrocarbons disappeared at 1000° C. The stability of methane was well illustrated here. It was found that the decomposition of methane was practically complete in 90 seconds at 1000° C.

H. Hollings and J. W. Cobb[2] conducted valuable experiments on the stability of methane. Mixtures of methane and hydrogen were passed through an electrically heated tube. At 800° C. with a mixture of equal parts of methane and hydrogen it was found that only 2 per cent of the methane was decomposed on passing the gases when the time of heating was one minute. At 1100° C., 65 per cent of the methane in a similar mixture was decomposed when the duration of the heating was 47 seconds. Thus methane is not greatly affected at 800° C., but is rapidly decomposed at 1100° C.

The work of Whitaker and Alexander[3] showed that methane was the last gas to be decomposed at temperatures from 1400° to 1600° C. With oil feed rates of 10 cc. per minute the illuminants disappeared at 1400° C., whereas 3.5 per cent of methane escaped destruction.

Lewes[4] passed methane through a platinum tube, six inches of which was heated to 1000° C. Unsaturated hydrocarbons, to the extent of 2.7 per cent, and 1.8 per cent acetylene formed. He concluded that the acetylene was formed in accordance with the reaction $2CH_4 \longrightarrow C_2H_2 + 3H_2$. In another paper Lewes[4] stated that methane when heated to 900° C. underwent practically no change.

Bone and Coward[5] found that at 700° C. the decomposition of methane was inappreciable. In an experiment at 785° C., with an open tube, they found that 91.6 per cent of the methane used was unchanged at the end of one hour, the rest of the gas being hydro-

[1] *Stahl u. Eisen*, **33** (1913), 239–45.

[2] *Gas World*, **60** (1914), 879–884.

[3] *J. Ind. Eng. Chem.*, **7** (1915), 484–495.

[4] *J. Chem. Soc.*, **61** (1892), 322–338; *Proc. Roy. Soc.*, **55** (1894), 90; **57** (1895), 394.

[5] *J. Chem. Soc.*, **93** (1908), 1197–1225.

gen. No one of the other hydrocarbons exhibited any such stability at these temperatures. Experiments were conducted at 1000° and at 1150° C., from the results of which the authors concluded that the normal decomposition of methane was into carbon and hydrogen. This they believed to be a surface effect almost exclusively. Only very small amounts of acetylene and olefins were found in the first few minutes of the heating. That acetylene or olefins were not the primary products of the decompositions which then undergo decomposition into carbon and hydrogen, Bone and Coward believe was proved by the nature of the carbon deposit. When methane decomposed, the carbon was of a peculiarly hard and lustrous variety, while acetylene and ethylene gave a soft dull variety.

In summing up the work on methane it can be said that the chief reaction is the decomposition into carbon and hydrogen, $CH_4 \longrightarrow C + 2H_2$, and that the reaction suggested by Lewes and Berthelot, $2CH_4 \longrightarrow C_2H_2 + 3H_2$, takes place to a small extent only.

Under the conditions of operation of a carbureted water gas set very little methane is decomposed. Though the temperatures of the retort walls in coal gas manufacture are much higher than those in the interior of the carbureter and superheater of a water gas set it is obvious that the gases do not reach the temperature of the refractory surfaces. So again methane is not decomposed to a large extent.

REACTIONS OF ETHANE

H. Hollings and J. W. Cobb[1] passed a gas of the composition 4.2 per cent ethane, 47.5 methane, and 48.3 hydrogen through an electrically heated porcelain tube. At 800° C., the exit gases had the composition 0.9 per cent ethane, 48.9 methane, 48.9 hydrogen, 1.3 ethylene, and a trace of acetylene. Thus the decomposition of ethane took place to an extent of 79 per cent under these conditions with a time of heating of 47 seconds. At 1100° C. the decomposition was 88 per cent. It is evident that ethane decomposes to ethylene, methane, and hydrogen. No mention was made of the separation of carbon, but on the other hand the gases passed through a tube filled with coke and the separation of carbon might not have been noticed.

[1] *Gas World*, **60**, 879–884.

Lewes[1] passed ethane through a platinum tube, and obtained in the resulting gases 19.5 per cent unsaturated hydrocarbons and 8.2 per cent acetylenes. When ethane diluted with 80 per cent hydrogen was heated with 15 per cent air, Lewes found 7.7 per cent unsaturated hydrocarbons, and 3.9 per cent acetylenes. He believed that ethane first broke down to ethylene and hydrogen, and that the ethylene gave rise to the acetylene.

Bone and Coward[2] showed that the primary reaction which ethane underwent when heated was a dissociation into ethylene and hydrogen: $C_2H_6 \rightleftharpoons C_2H_4 + H_2$. In the gases from the decomposition of ethane they found the ratio of the methane to the hydrogen to be about 2 : 1, whereas if it is considered that the ethylene formed as shown in the equation above decomposes thus—$C_2H_4 \longrightarrow CH_4 + C$—the ratio of methane to hydrogen in the gaseous products from the decomposition of ethane should be 1 : 1. This can be explained only on the basis of the assumption that some of the hydrogen enters into combination, forming methane or products which by their subsequent decomposition give methane. Bone and Coward suggested that it was due to the hydrogenation of such residues as $—CH_3$, $=CH_2$, $\equiv CH$, which can be thought of as having fugitive existence. Their results in this connection are further discussed under our caption "Atmospheres of Hydrogen."

However, "substances" such as $—CH_3$, $=CH_2$, and $\equiv CH$ are in a class with "nascent" hydrogen. The high methane content of these resultant gases can be explained if we give credence to the possibility of reactions such as $C_2H_6 + H_2 \rightleftharpoons 2CH_4$. This seems the more probable when we call to mind that small amounts of acetylene and ethylene are found in the gases which result from the heating of methane as was shown by Lewes. The acetylene and ethylene would come from the ethane formed as in the equation above.

Bone and Coward found only small amounts of acetylene in the gases from the decomposition of ethane, nor did the formation of aromatic hydrocarbons take place to a large extent. At 800° C., with one minute heating, only 17.9 per cent ethane survived. The decomposition of ethane was not believed to be a surface effect.

[1] *J. Chem. Soc.*, **61** (1892), 322–338.
[2] *Ibid.*, **93** (1908), 1197–1225.

Day,[1] in summing up the work of Fourcroy, De-Wilde, Buff, Hoffman, Berthelot, Marchand, Grove, and Magnus, says: "It seems clear that at the highest temperatures ethylene separates directly into its elements. Below this point marsh gas and carbon are obtained ($C_2H_4 \longrightarrow CH_4 + C$), then marsh gas and several liquid products, among them benzene, styrene, etc., under certain conditions." Day circulated ethylene through a glass tube heated to various temperatures for different lengths of time. No change in volume was observed with 14 hours' heating at 300° C. At 344° C., a contraction of one-twentieth of the original volume took place in 24 hours, and Day concluded that condensation had taken place, for no methane or hydrogen was found in the gas. At 400° C., 132 cc. of ethylene contracted to 63 cc. in 171 hours. No hydrogen was present in the final gas, which was a mixture of 22.4 cc. methane, 24.8 cc. ethane, and 15.6 cc. ethylene or other olefins.

Norton and Noyes[2] passed ethylene slowly through a glass tube heated to a low red heat for 60 cm. of its length. The products passed out through a series of U-tubes immersed in a freezing mixture, then through ammoniacal cuprous chloride, through bromine, and finally to a gasometer. Carbon was deposited in the tube. From the liquid condensing in the freezing mixture benzene and naphthalene were isolated. Only traces of acetylene were in the gases, and the authors concluded that if acetylene were formed it must have been decomposed in the tube. The liquid bromides collected consisted chiefly of ethylene dibromide, but also contained some methylene dibromide, propylene dibromide, and butylene dibromide. The solid bromides had the composition $C_4H_6Br_4$, and Norton and Noyes believed that it could be explained by the reaction $2C_2H_4 \longrightarrow C_4H_6 + H_2$. The gases collected consisted of methane and ethane.

Sabatier and Senderens[3] passed pure dry ethylene over freshly reduced nickel at 300° C. and upwards. The products were carbon, hydrogen, methane and ethane in varying proportions. These investigators found that the hydrogen increased with increase in temperature, and believed that it resulted from a secondary reaction, *i. e.*, decomposition of methane

[1] *Am. Chem. J.*, **8** (1886), 153–167.
[2] *Ibid.*, **8** (1886), 362–364.
[3] *Compt. rend.*, **124** (1897), 616–618.

into carbon and hydrogen. In a later paper[1] similar decompositions were carried out with cobalt as the catalyst. The analysis of a typical gas which resulted was: ethylene, 67.4; ethane, 13.4; methane, 4.4; and hydrogen 14.8 per cent. As would be expected, if the methane equilibrium is kept in mind, the decomposition of the methane in the presence of the catalyst was quite extensive, and a fairly large proportion of the hydrogen so formed reacted with the ethylene to form ethane.

Bone and Wheeler,[2] in their study of the combustion of ethylene, found that when insufficient oxygen was present to burn the ethylene to formaldehyde a thermal decomposition took place. The products were carbon, hydrogen, methane, and traces of acetylene. Ipatiew's study of the condensation reactions of the ethylene hydrocarbons has been discussed under the secondary decomposition, but should be called to mind again here. Engler also has laid emphasis on the importance of such condensation reactions.

Pring and Fairlie[3] found that small amounts of ethylene were formed from carbon and hydrogen; and that the ethylene so formed reacted further to give methane.

H. Hollings and J. W. Cobb[4] passed a gas mixture containing 10.6 per cent ethylene, 47.7 methane, and 41.7 hydrogen through a tube heated to 800° C. The exit gases, with a heating time of 45 seconds, contained 4.5 per cent ethylene, 54.4 methane, 40.3 hydrogen and 0.8 acetylene. No benzene or ethane were found. Methane and acetylene appeared to be the chief products. Apparently the reactions taking place were: $C_2H_4 \longrightarrow CH_4 + C$ and $C_2H_4 \longrightarrow C_2H_2 + H_2$. The first of these was much the most important reaction. A contraction in volume took place which the authors believed was due to the formation of liquid products. At 1100° C. the ethylene was decomposed completely in 35 seconds' heating.

Lewes[5] found that ethylene yielded considerable proportions of acetylene when it was decomposed by heat. From a study of the gases made from Russian oil he concluded that nothing happened till a

[1] *Compt. rend.*, **131**, iv (1900), 267–270.
[2] *J. Chem. Soc.*, **85** (1904), 1637–1663.
[3] *Repts. 8th Int. Congress Applied Chem.*, **21**, 65, *et seq.*
[4] *Gas World*, **60**, 879–884.
[5] *J. Chem. Soc.*, **61** (1892), 322–338; *J. Soc. Chem. Ind.*, **11** (1892), 584–590; *Proc. Roy. Soc.*, **55** (1894), 90; *Trans. Inc. Inst. of Gas Eng.*, **10** (1900), 111–133.

temperature of 800° C. was reached, but that then the ethylene began to decompose in accordance with the equation $3C_2H_4 \longrightarrow 2C_2H_2 + 2CH_4$.

The experiments of Bone and Coward, however, completely disproved any such mode of decomposition for ethylene. From their work[1] it appeared that ethylene decomposed in different ways at different temperatures. In the study of the thermal decomposition of ethane at 675° C., it was shown that the ethane dissociated first into ethylene and hydrogen, and that the further change consisted largely in the breaking down of the ethylene into carbon and hydrogen. When the reactions undergone by pure ethylene at 575° C. were studied it was found that very complex gas mixtures were obtained. Acetylene, ethane, methane, hydrogen and aromatic hydrocarbons were all present in notable quantities while the separation of carbon was small. The experiments continued over a time of 150 minutes and there was a continuous decrease in the volume of the gases which indicated a formation of aromatic hydrocarbons.

Bone and Coward regarded acetylene as one of the primary decomposition products of ethylene at the temperature of 575° C. The large percentage of hydrogen without a corresponding separation of carbon precluded Lewes' contention that the acetylene arose largely from the reaction $3C_2H_4 \longrightarrow 2C_2H_2 + 2CH_4$, for, were this the main reaction, hydrogen would result from the secondary decomposition of the acetylene which is of necessity accompanied by separation of carbon. Experiments were conducted at 700°, 800° and 950° C. The higher the temperature the greater the separation of carbon, and the smaller the formation of aromatic hydrocarbons. Acetylene and ethane were produced in smaller amount, but methane in larger amount.

Bone and Coward have some difficulties in reconciling their results on the study of ethylene alone, with those of the ethylene resulting from the dissociation of ethane. The formation of acetylene is much greater and the decomposition into carbon and methane less with pure ethylene than with the ethylene resulting from the decomposition of ethane. It seems that the presence of the ethane and the hydrogen in the latter case are all-important.

SUMMARY—It appears that at temperatures up to 700° C. the dissociation of ethylene into acetylene

[1] *J. Chem. Soc.*, **93** (1908), 1197–1225.

and hydrogen is the most important reaction. Condensation also takes place to some extent. At higher temperatures the rate of the decomposition into carbon and methane is much greater, so this reaction plays an important part. The high proportion of methane found by Bone and Coward at temperatures of about 800° C., and explained by them as due to hydrogenation of unsaturated residues can be understood if it is assumed that reactions such as $C_2H_4 + 2H_2 \rightleftarrows 2CH_4$ take place.

REACTIONS OF ACETYLENE

It has been seen that acetylene is formed by the dissociation of ethylene. Many authors have noted its formation in the gases made from oil.

Lewes[1] has shown that acetylene was present in the gases made from Russian petroleum at 700° to 1000° C., and that the amount increased with the temperature. The percentages were 0.084 at 700°, 0.38 at 800° and 0.46 at 900° C.

Haber and Oechelhauser[2] claimed to have found 1.10 per cent acetylene in gases made from hexane at temperatures between 900° and 1000° C.

Worstall and Burwell[3] reported 11.8 per cent in the gases from the decomposition of heptane and octane under the conditions of Pintsch oil gas manufacture. The presence of this amount of acetylene, however, in the light of the work of all other investigators, is open to confirmation; *e. g.*, ammoniacal cuprous chloride was used to absorb the acetylene while it is known that this reagent will absorb ethylene as well.

W. A. Noyes, W. M. Blinks and A. V. H. Morey[4] found acetylene in the oil gases made at 900° to 1000° C. as indicated by the precipitate obtained when the gases were passed through ammoniacal cuprous chloride. The observation of these investigators, and many more which might be mentioned, rather overbalance the claim of Norton and Andrews[5] that they could not obtain acetylene in the gases made by passing the vapors of pentane and hexane through a porcelain tube heated to bright red heat. It is apparent, therefore, that the reactions of acetylene are of some moment to the gas manufacturer.

[1] *J. Soc. Chem. Ind.*, **11** (1892), 584–590.

[2] *J. Gasbel*, **39** (1896), 377–382, 395–399, 435–439, 452–455, 799–805, 813–818, 830–834.

[3] *Am. Chem. J.*, **19** (1897), 815–845.

[4] *J. Am. Chem. Soc.*, **16** (1894), 688–697.

[5] *Am. Chem. J.*, **8** (1886), 1–9.

R. Meyer[1] made a study of the thermal reactions of acetylene. If the gas alone was passed through an electrically heated tube at 650° to 800° C. the acetylene was decomposed into carbon and hydrogen. If hydrogen was mixed with the acetylene this decomposition was avoided. The gases leaving the apparatus contained some methane. The tar yields were high, in one case 60 per cent of the weight of the acetylene used, showing the decided tendency of acetylene to condense to higher molecular weight compounds. Twenty per cent of the tar, by weight, was composed of benzene. Naphthalene, anthracene, indene, toluene, diphenyl, fluorene, pyrene and chrysene were also detected. Meyer's conclusion was that the condensation of acetylene was an essential, though not the sole, factor in the formation of the aromatic components of coal tar.

Not all investigators have agreed that benzene is formed from acetylene.

Norton and Noyes,[2] in their experiments on ethylene, found only small amounts of acetylene in the gases, and yet the liquid products contained fair amounts of benzene. These authors said that if benzene was formed from acetylene the conditions of their experiments, *i. e.*, low red heat, must have been just those favorable for this reaction of condensation.

Lewes[3] was of the opinion that acetylene when heated, as in the coal gas retorts, condensed at once to benzene and other aromatic hydrocarbons. At higher temperatures it was decomposed into its elements, and this according to Lewes, was the only reaction resulting in the separation of carbon.

Berthelot[4] had previously announced similar views. He passed acetylene through glass tubes at low temperatures and obtained solid and liquid hydrocarbons among which were benzene, naphthalene, and styrene.

Jacobson[5] believed that acetylene condensed to benzene, and that the substituted acetylenes gave rise to toluene, xylenes and mesitylene.

Anschütz[6] pointed out that if it was considered that a hydrogen molecule split out the formation of naphthalene could be accounted for: $5C_2H_2 \longrightarrow C_{10}H_8 + H_2$.

[1] *Ber.*, **45** (1912), 1609–1633.
[2] *Am. Chem. J.*, **8** (1886), 362–364.
[3] *Trans. Inc. Inst. of Gas Engineers*, **10** (1900), 111–113.
[4] *Ann. chim. phys.*, **9**, iv, 445, 469.
[5] *Ber.*, **10** (1877), 855.
[6] *Ibid.*, **11** (1878), 1215.

Haber found that benzene and some naphthalene were formed by passing acetylene through a tube at 700° C.

Sabatier and Senderens[1] studied the action of the metals copper, nickel, cobalt, platinum, and iron on acetylene. At temperatures of 150° to 250° C. a large part of the liquid products formed were aromatic hydrocarbons. Decomposition into carbon and hydrogen also took place, and nearly all the hydrogen so liberated combined with the acetylene to form ethylene and ethane.

Bone and Coward[2] showed that at 500° C. the principal change undergone by acetylene was condensation, with decomposition into its elements second in importance, while hydrogenation to ethylene, ethane, and methane was least important. At 600° C. the relationship was found to be much the same. At 800° C. the gas "flashed," and the temperature locally was much higher than 800° C. The most important feature of the results at this temperature was the higher proportion of methane in the resultant gases. This could be accounted for, according to Bone and Coward, only by assuming the hydrogenation of $\equiv CH$ residues formed momentarily by the breaking across a triple bond. They strengthened this argument by heating acetylene in nitrogen and hydrogen, in the ratio of $C_2H_2 + 3N_2$ and $C_2H_2 + 3H_2$, when it was found that five times as much methane was formed when the gas was cracked in hydrogen as when the change took place in nitrogen. Condensation occurred at 800° C., but far less extensively than at lower temperatures. At 1100° C. condensation played a still less important part, decomposition into the elements being the chief change. The most favorable temperatures for the condensation of acetylene lay between 600° and 700° C.

SUMMARY—It would appear, then, that at temperatures up to 700° C. acetylene undergoes a fairly rapid condensation to benzene and its homologs. Decomposition into carbon and hydrogen is second in importance at these temperatures while hydrogenation to ethylene, ethane and methane is least important. At slightly higher temperatures the importance of condensation diminishes, while the decomposition into the elements and hydrogenation both increase. At still higher temperatures, such as 1100° C., the

[1] *Compt. rend.*, **131**, iv (1900), 267–270.

[2] *J. Chem. Soc.*, **93** (1908), 1197–1225.

decomposition into carbon and hydrogen is the important reaction.

REACTIONS OF PROPYLENE, DIOLEFINS, SUBSTITUTED ACETYLENES, PROPANE, AND HIGH MOLECULAR WEIGHT TARRY COMPOUNDS

No discussion of the pyrogenic reactions of pyropylene, diolefins, substituted acetylenes, propane, and high molecular weight tarry compounds was found. A few conjectures as to their probable reactions may at least be of interest.

PROPYLENE can condense to form substituted naphthenes. It has been established that such a reaction does take place in the case of ethylene, and it is entirely probable that propylene undergoes condensation as readily or more readily than ethylene. A rupture of the propylene molecule with formation of acetylene and methane is also not an improbable reaction:

$$CH_3 — CH{=}CH_2 \longrightarrow CH_4 + CH{\equiv}CH$$

The DIOLEFIN which has most frequently been isolated and identified from the products of the thermal decomposition of hydrocarbons is divinyl or vinyl ethylene, $CH_2{=}CH—CH{=}CH_2$. Whether it is formed in small amount only, or whether it is formed in large amount as an intermediate product between the higher olefins and more complex condensation products cannot be definitely stated. Isoprene, a diolefin of the supposed formula $CH_2{=}C(CH_3)—CH{=}CH_2$, is known to condense spontaneously to dipentene, and ultimately into caoutchouc. If judgment from analogy is allowable it would seem that divinyl would also condense readily. This rapid condensation, rather than a small formation, may be responsible for the fact that divinyl is found in small amount only in the products of hydrocarbon decomposition.

It may be regarded as well established that *acetylene* will condense to form benzene if passed through a tube heated to 600° to 750° C. So it would be probable that the substituted acetylenes would undergo similar reactions with formation of substituted benzenes. That such reactions actually take place is rendered the more plausible by the observation of Rittman and his collaborators, referred to under the discussion of aromatic hydrocarbons in this paper, that the substituted benzenes, such as cymene, xylene, and toluene,

are the first to be formed when paraffin hydrocarbons are decomposed pyrogenically.

PROPANE may easily decompose into methane and ethylene, thus, $CH_3CH_2CH_3 \longrightarrow CH_4 + CH_2 = CH_2$. This reaction is analogous to the primary reaction of the higher paraffin hydrocarbons.

The HIGH MOLECULAR WEIGHT TARRY COMPOUNDS have been built up by synthetic reactions. For this reason they are no doubt fairly stable compounds as regards the influence of heat, and in general pass on through the apparatus and into the tar. Haber has suggested that the chief reaction of the compounds of this class is a splitting off of hydrogen.

IV—AROMATIC HYDROCARBONS—THEIR FORMATION AND REACTIONS

Though the formation of aromatic hydrocarbons takes place only to a limited extent in water gas machines, and to but a slightly greater extent in coal gas retorts, the tars from these processes are important sources of the commercial aromatic hydrocarbons.

The aromatic hydrocarbons contribute greatly to the illuminating value of a gas as determined in an open flame burner. However, should the calorific standard for gas service in the course of time become general, the presence of the aromatic compounds in the gas would be of far less importance to the gas manufacturer than it is to-day. These compounds contribute less to the heating value of the gas than the compounds from which they are formed. Their chief importance would then lie in the better prices obtainable for the tars containing them.

Notwithstanding these facts it is deemed well worth while to discuss to some extent the literature relevant to the formation of the aromatic hydrocarbons, and the changes undergone by them.

Lewes,[1] in commenting on Armstrong's statement[2] that benzene was not formed from acetylene, said that he believed this reaction to be responsible for a part, only, of the benzene formed and that the polymethylene hydrocarbons, by their dissociation into benzene and hydrogen, contributed largely. The high percentage of benzene (20 per cent) in Russian oil tars was cited as proof.

It was suggested by Armstrong and Miller[3] that hexane might have a specific tendency to condense

[1] *J. Soc. Chem. Ind.*, **11** (1892), 584–590.
[2] *Ibid.*, **3** (1884), 462–468.
[3] *J. Chem. Soc.*, **49** (1886), 74–93.

to hydro-aromatic hydrocarbons which in turn would give rise to benzene. This has been disproved by Haber;[1] approximately equal amounts of benzene were found in the reaction products of hexane and trimethylethylene. The latter compound could not form benzene by a linking together of the ends of its carbon chain.

Considerable recent work has been done with the commercial production of aromatic hydrocarbons as its object. Though these investigations have not been made from the manufacturer's gas viewpoint, valuable conclusions as to the mechanism of the reactions of the aromatic hydrocarbons can be drawn from them.

Brooks and Humphreys[2] discussed the presence of aromatics in high boiling petroleum distillates. Though they recognized that in oil gas making benzene no doubt results from the polymerization of acetylene they did not believe that such condensations were responsible for the benzene in their distillates since the temperature of distillation did not exceed 420° C.—at which temperatures they assumed acetylene formation negligible. However improbable such formation of acetylene may be, it has not been proved that it does not take place. These authors also referred to the work of Ogloblin,[3] in which it was shown that at temperatures of 525° to 550° C., Russian naphtha (a hydrocarbon largely composed of naphthenes) broke down readily to give good yields of benzene, toluene, xylene, and smaller amounts of naphthalene and anthracene. Brooks and Humphreys referred to this work in the sense that the temperatures of 525° to 550° C. were the lower limiting temperatures at which these reactions would take place. Ogloblin, however, intended to convey no such impression, and stated that at these temperatures the reactions took place readily. This fact convinces us that Brooks and Humphreys were in no sense justified in their conclusion that the benzene in their high boiling petroleum distillates arose from hydrocarbons containing a phenyl radical.

The work of Engler and Lehmann[4] can be mentioned in this connection. These investigators found naphthenes and aromatic hydrocarbons in oily distillates

[1] *J. Gasbel,* **39** (1886), 377–382, 395–399, 435–439, 452–455, 799–805, 813–818, 830–834.

[2] *J. Am. Chem. Soc.*, **38** (1916), 393–340.

[3] *Z. angew. Chem.*, **18** (1905), 540.

[4] *Ber.*, **30** (1897), 2365–2368.

made by heating fats under pressure at temperatures below those used by Brooks and Humphreys.

It must be kept in mind also that Rittman and his co-workers have obtained maximum yields of benzene at temperatures of 600° C. and slightly above and 4 atmospheres pressure. They are of the opinion that condensation of acetylenes, dehydrogenation of naphthenes, and splitting of polycyclic or asphaltic hydrocarbons all contribute. Egloff and Twomey[1] obtained considerable yields of benzene at 450° C. and atmospheric pressure.

An excellent investigation of the relationships between the most important aromatic hydrocarbons has been made by Rittman, Byron, and Egloff[2] and by Rittman and Egloff.[3] They used the pure hydrocarbons cymene, xylene, toluene, benzene, naphthalene, and anthracene, which were treated at various temperatures and pressure in the furnace formerly used by Whitaker and Rittman.[4] The authors came to the conclusion that from cymene it was possible to produce all the other hydrocarbons mentioned. Xylene gave toluene, benzene, naphthalene, and anthracene, but no cymene. Toluene gave benzene, anthracene, and naphthalene, but no cymene or xylene. Only naphthalene and anthracene may be produced from benzene. Naphthalene yielded anthracene but none of the others. Anthracene yielded only carbon and gas. The authors noted that other compounds such as diphenyl, methylnaphthalenes, and anthracenes, and phenanthrene were formed to some extent. It can be seen that the general course of the reactions with monocyclic aromatic compounds was from higher to lower molecular weight compounds, and that the tendency was for monocyclic to go to polycyclic compounds.

The influence of various conditions on the formation of aromatic hydrocarbons has recently been reviewed by Egloff and Twomey.[5] This paper also records the results of an investigation of the effect of temperature on the individual aromatic hydrocarbon formation at atmospheric pressure. Temperatures of 450° to 600° C. produced more toluene and xylene than benzene in the cracked oil, and more toluene than xylene. More toluene than benzene was formed at

[1] *J. Phys. Chem.*, **20** (1916), 121, *et seq.*
[2] *J. Ind. Eng. Chem.*, **7** (1915), 1019, *et seq.*
[3] *Met. Chem. Eng.*, **14** (1916), 15–18.
[4] *J. Ind. Eng. Chem.*, **6** (1914), 383, 472.
[5] *J. Phys. Chem.*, **20** (1916), 121–150.

650° C., and more benzene than xylene. No naphthalene or anthracene was found in the recovered oils at 650° C. In the temperature range of 700° to 875° C. more benzene was formed than toluene or xylene, but more toluene than xylene. At 750° C. naphthalene began to be formed, and at 800° C. anthracene formation commenced. The amounts of both of these hydrocarbons increased with temperature. The authors seemed justified in their conclusion that the individual aromatic formation with change of temperature was as follows:

HIGHER HOMOLOGS such as mesitylene pseudocumene, etc. ⟶ TOLUENE AND XYLENE ⟶ BENZENE

This is not to be interpreted, for instance, to mean that toluene and xylene cannot form anthracene or naphthalene directly.

THE REACTIONS OF BENZENE have been the subject of a number of investigations, and it is deemed worth while to present them here in review. Schultz[1] found that diphenyl was formed by passing benzene vapors through tubes heated to redness. Meyer,[2] in his paper on the condensations of acetylene, noted the presence of diphenyl in the high boiling fractions of the liquid obtained by passing acetylene through heated tubes. Ipatiew[3] found that diphenyl was not formed below 600° C. Smith and Lewcock[4] passed benzene vapors through a heated iron tube at the rate of 5 cc. of liquid benzene per minute. The yield of diphenyl was not increased by the use of temperatures above 720° C. The time factor was found to be important. By the variance of conditions yields of diphenyl ranging from 0.0 to 59 per cent could be obtained. H. Hollings and J. W. Cobb[5] found that the decomposition of benzene at 800° C. was negligible when a mixture of practically equal amounts of methane and hydrogen saturated with benzene vapor was passed through a heated tube. At 1100° C., no trace of the benzene could be found in the products. According[6] to Haber, benzene was not decomposed by heat at temperatures below 900° C. Above 1000° C.,

[1] *Ber.*, **9** (1876), 547.
[2] *Ibid.*, **45** (1912), 1609–1633.
[3] *J. Russ. Phys. Chem. Soc.*, **39** (1907), 681.
[4] *J. Chem. Soc.*, **101** (1912), 1453–1458.
[5] *Gas World*, **60** (1914), 879–884.
[6] *J. Gasbel*, **39** (1896), 377–382, 395–399, 435–439, 452–455, 799–805, 813–818, 830–834.

however, it was affected; diphenyl and crystalline substances not further examined were found; naphthalene was not observed.

The great variation in the results of these authors shows very well the great influence of conditions on the reactions of benzene. Temperature, pressure, and time of heating are extremely important.

SUMMARY—The reactions responsible for the aromatic hydrocarbons formed in the pyrogenic decomposition of hydrocarbon oils are

1—Condensation of acetylenes
2—Dehydrogenation of naphthenes
3—Decomposition of complex compounds already containing the phenyl radical

Toluene, xylene, ethyl benzene, and similar compounds are formed first and most easily. These by further change give rise to benzene, naphthalene, and anthracene. With high molecular weight monocyclic compounds the general course of the reaction is toward compounds of lower molecular weight. In general, monocyclic compounds tend to go to polycyclic compounds.

V—INFLUENCE OF ATMOSPHERES OF HYDROGEN AND INERT GASES ON THE PYROGENIC DECOMPOSITION OF HYDROCARBONS

The idea that an oil cracked in hydrogen or in inert gases gave more valuable products has been prevalent for many years.

Lewes[1] states that the better results are obtained by cracking oil in gases such as hydrogen, carbon monoxide, or water gas. According to Lewes these gases exerted their helpful influence by "separating and partly protecting the molecules during the decomposition by heat." Thus the temperature ranges over which good results could be obtained was increased, and excessive loss and breaking down of the hydrocarbons prevented. The use of blue water gas in coal gas retorts was also advocated.

Lewes[2] found a considerable increase in the illuminants formed per given weight of Russian oil when the oil was decomposed in atmospheres of inert gases. He also commented on the analogous results obtained by the use of the Lowe system, and was of the opinion that the blue water gas prevented the decomposition going too far, and also aided the breaking up of the

[1] *Trans. Inc. Inst. of Gas Engineers*, **2** (1892), 77–85.
[2] *J. Soc. Chem. Ind.*, **11** (1892), 584–590.

benzene. Lewes no doubt had in mind the fact that dilution, by diminishing the partial pressure of the acetylene, would tend to favor the acetylene side of the equilibrium $3HC{\equiv}CH \rightleftarrows C_6H_6$.

Numerous patents on the various methods of using hydrogen or inert gases as an aid to the decomposition of oils have been issued. The patents of H. Blau[1] are illustrative: these involve a manufacture of oil gas by "expansion and rarefaction with permanent gases," whereby the separation of soot, and the consequent irregularities of working were avoided.

W. Benthrup[2] patented a process for the introduction of water gas into coal gas retorts during the early stages of the gasification. The gas yield was supposedly increased, and a better quality of gas obtained.

H. Croissant[3] discussed at some length the introduction of water gas into coal gas retorts. The advantages according to him are the increase in the gas yield from the coal, and a gain in heating value of 7 to 12 per cent. The tar was more fluid, and stoppages in the ascension pipes were less frequent. Both of these latter points show a less destructive cracking of the hydrocarbons distilled from the coal. The water gas should be introduced in the proportion of $^1/_2$ to 1 volume for every 2 volumes of coal gas during the first 2 hours of the period of carbonization.

The basis of the Del Monte process of carbonization[4] developed in England and was the recirculation of the permanent gases (such as hydrogen and methane) through the coal gas retorts. Excessive cracking of the high hydrocarbons distilled out at moderate temperatures was thus prevented.

Meyer's work, in which it was found that admixture of hydrogen with acetylene prevented the decomposition of the latter into carbon and hydrogen, has already been mentioned.

Several other authors have mentioned the effects of decomposing oils in water gas. Thus C. E. Munroe stated that the hydrogen in the water gas had the effect of increasing the olefins and diminishing the amount of tar. A. E. Forstall[6] was of the belief that the presence of water gas arrested the decomposition

[1] French Pat. 332,115, **1903**, and Ger. Pat. 258,610, **1912**.

[2] Ger. Pat. 157,470, **1903**.

[3] *J. Gasbel*, **47** (1904), 219-222.

[4] *Gas World*, **58** (1913), 321, 328, 430 and 477; *J. Gas Lighting*, **120** (1913), 370.

[5] *J. Frank. Inst.*, **174** (1912), 1–33.

[6] *Ibid.*, **174** (1912), 279–302.

of the hydrocarbons before carbon was deposited, and thus allowed the use of a larger surface of contact for heating. Thomas Holgate[1] pointed out that the curve for the rate of decomposition of methane with increase of temperature had a maximum, and ascribed this to the retarding effect of the increasing amounts of hydrogen formed by the decomposition.

Redding[2] cited several average analyses of water gas. These are shown in abbreviated form in the following table, but calculated to an illuminants-carbon-monoxide-methane-hydrogen basis.

No.	Illuminants	Methane	Carbon Monoxide	Hydrogen
1	10.4	19.9	33.6	36.1
2	11.9	21.3	33.2	33.6
3	14.5	14.0	35.1	36.4
4	14.5	17.8	32.2	35.5

Keeping in mind that the water gas introduced has a little more hydrogen than carbon monoxide it can be seen that the proportion of hydrogen to carbon monoxide has not been much increased. The average analysis of Pintsch gas for hydrogen is 14 per cent, but evidently the oil when cracked in the water gas has not given rise to this amount of hydrogen. This appears as good evidence, since the other reactions which might tend to distort the carbon monoxide-hydrogen ratio, namely, $2C + O_2 \rightleftarrows 2CO$; $CO + HOH \rightleftarrows CO_2 + H_2$; and $CO_2 + C \rightleftarrows 2CO$, tend to a balance, and in any case do not have a large effect.

A study of the gasification of oils in hydrogen and other gases was made by Hempel. In his experiments the oil was gasified and led into a 16-in. tube heated by a row of Bunsen burners. The rate of gasification was 1.6 to 2.0 grams of oil per minute. The gases contained from 30 to 36 per cent unsaturated hydrocarbons, 47.5 to 51 per cent saturated hydrocarbons, and 14 to 17 per cent hydrogen. The products of decomposition of the oil and the hydrogen reacted as was evidenced by the 15 per cent diminution in total volume when the hydrogen was introduced in the proportion 1 hydrogen : 2 oil gas. The resultant gases were practically identical with those produced by cracking oil alone, but the yields of methane, ethylene, and ethane, according to Hempel, were increased per unit weight of oil. The ethane particularly was increased. The gases showed a 15 per cent gain in heat of combustion over the simple oil gases. The tars

[1] *J. Gas Lighting*, **106** (1909), 25–28, 84–86.

[2] *Progressive Age*, **24** (1906), 485.

formed were more fluid, and in smaller amount by about 10 per cent when the oils were cracked in hydrogen. The separation of carbon was also less by about 1.5 to 3.0 per cent. The experiments indicated that when the hydrogen reached a proportion of 50 to 60 per cent of the final gas the formation of gaseous hydrocarbons was confined to a limited quantity. When hydrogen was used in the proportion of 1 hydrogen : 1 oil gas, there was a falling off in the production of ethane and much of the hydrogen was lost in the tars, which increased in amount. The most favorable amount of hydrogen is about 18 cu. ft. per pound of oil. The opinion was expressed that the 15 per cent hydrogen normally present in oil gas exerts a considerable influence. From a very limited investigation Hempel concluded that the cracking of oils in atmospheres of nitrogen or carbon monoxide caused no change in the volume of gas produced from the oil, nor in the candle power. The secondary decomposition was diminished and as a result the percentage of methane falls a little and the olefin percentage increases.

E. C. Jones[1] and Z. B. Jones[2] have carried out experiments on an all-oil water gas set to determine the effect of the cracking of oils in inert gases, and also the extent to which carbon monoxide and hydrogen react under working conditions to form methane. They established that the inert gases had the effect of increasing the proportion of carbon in the gas per unit weight of the oil, and in their technical operations cracked the oil in an atmosphere of gas from their holder, with beneficial effect. Their experiments showed, too, that carbon monoxide and hydrogen united to some extent to form methane and water.

Whitaker and Rittman[3] noted that the quantity and quality of the gas formed from the oil increased when the oil was cracked in atmospheres of hydrogen, and that the tar and deposited carbon decreased. They found that more hydrogen entered into combination with the decomposition products of the oil at atmospheric pressure than at a pressure of 0.75 pound absolute.

The results obtained by the cracking of oil in atmospheres of hydrogen may be ascribed to at least three factors:

[1] *Am. Gas Lighting, J.*, **92** (1910), 437–445.
[2] *Progressive Age*, **28** (1910), 373.
[3] *J. Ind. Eng. Chem.*, **6** (1914), 472–479.

1—*The dilution effect*, which is the same as diminishing the partial pressures of all the reacting gaseous hydrocarbons.

2—*The increase in volume*, whereby the time of heating of the hydrocarbon molecules is less than in the making of straight oil gas.

3—*Hydrogenation of hydrocarbons.*

The first of these factors indicates that cracking oils in hydrogen or other gases should favor those reactions which result in greater numbers of molecules: *e. g.*, the tendency of acetylene to condense to benzene would be less in hydrogen than if the acetylene were present alone. The diminution of the time of heating would result in a less extensive decomposition of the various hydrocarbons. The products obtained should be those of the earlier stages of hydrocarbon decomposition rather than the large amounts of methane, hydrogen, and aromatics which are obtained by very extensive changes. The extent to which hydrogenation is important can be better judged by considering the experimental work which bears directly on this factor. Some mention of this work has been made under our discussion of the secondary decomposition of hydrocarbons.

P. Sabatier and J. B. Senderens[1] passed acetylene and hydrogen over various catalysts at low temperatures. With cobalt as catalyst there was formed 26 per cent ethane, 70 hydrogen and 4 of a mixture of benzene vapor and unchanged acetylene. Nickel as catalyst gave even more ethane than cobalt, while iron was far less active, giving chiefly ethylene and its homologs.

C. Paal[2] found that acetylene was easily reduced to ethylene and ethane by hydrogen in the presence of colloidal palladium. If equal volumes of acetylene and hydrogen are taken an 80 per cent yield of ethylene will result.

Ipatiew's results[3] on the hydrogenation of terpene hydrocarbons and aromatic hydrocarbons with unsaturated side chain should also be mentioned. Various catalytic substances were used, and the hydrogen was introduced under 100 to 110 atmospheres pressure. The hydrogenation of the side chain took place at temperatures of 95° C. in the presence of NiO catalyzer,

[1] *Compt. rend.*, **124** (1897), 832.

[2] *Chem. Ztg.*, **36** (1912), 60, *et. seq.*

[3] *J. Russ. Phys. Chem. Soc.*, **43** (1911), 1754–1760; **45** (1913), 944–945; **45** (1913), 1829–1834.

while the aromatic nucleus was hydrogenated completely only at temperatures of 185° to 190° C. Though these results are interesting and valuable it must not be concluded from them that similar reactions would take place when these substances and hydrogen are heated together even though the temperatures are considerably higher.

Meyer[1] in his study of the pyrogenic reactions of acetylene passed mixtures of acetylene and hydrogen through a vertical tube furnace at temperatures of 650° to 800° C.: no appreciable formation of ethylene or ethane took place. Haber found 1.3 per cent ethylene in the gases resulting from passing a mixture of acetylene and hydrogen through a tube heated to 630° to 645° C. Lewes found that the hydrogenation of acetylene to olefins was an important reaction at 1000° C.

The noteworthy results of Bone and Coward[2] have already been mentioned under the discussion of the decomposition of ethane. To further validate their explanation of the high ratios of methane to hydrogen these authors decomposed mixtures of ethane and nitrogen in the proportion of 1 ethane : 3 nitrogen, and ethane and hydrogen in the proportion 1 ethane : 3 hydrogen under identical conditions. The ratio of methane to hydrogen in the gases from the methane nitrogen mixture had the approximate value of unity, while from the ethane-hydrogen mixtures it was much higher, showing a considerable hydrogenation of the decomposition products of the ethane; 2.27 times as much methane was formed in the hydrogen atmosphere as in the nitrogen atmosphere. Similar experiments were carried out with ethylene and nitrogen, and ethylene and hydrogen. The results obtained were entirely analogous to those of the acetylene experiments. The ratio of the methane formation in the hydrogen atmosphere to that in the nitrogen atmosphere was 3.15 : 1.

Bone and Coward have shown that both ethylene and acetylene have a certain tendency to combine with hydrogen at low temperatures, but that the importance of these reactions is never very great, and that they are insignificant above 1000° C.

In so far as the work of these several investigators allows us to draw conclusions it seems that hydrogenation of hydrocarbons such as ethylene and acetylene

[1] *Ber.*, **45** (1912), 1609–1633.
[2] *J. Chem. Soc.*, **93** (1908), 1197–1225.

does take place, but that it is never a reaction of great importance. The fact, however, that hydrogen is actually absorbed when oils are cracked in atmospheres of the gas shows that hydrogenation of some sort takes place. Possibly the higher unsaturated hydrocarbons are hydrogenated more readily. The evidence from our experiments in this connection is presented elsewhere in this paper.

VI—TRANSFER OF HEAT IN GAS MACHINES

The most striking feature of the literature which records the result of investigations of hydrocarbon decompositions is the great difference between the results of various investigators who report that they have worked at the same temperature, and, in general, under the same conditions. Irregularities too great to be attributed to the personal equation are of frequent occurrence, and these are in need of explanation.

It is often suggsted that these differences are caused by the catalytic effects of the materials of construction, but without doubt the catalytic effect of contact surfaces has been overestimated. It is well known from general experience that these surfaces are always covered with a layer of hard carbon as a result of the decomposition of hydrocarbons. Hence the gases do not come into contact with an active material, but rather into contact with a dense layer of carbon deposit which is inactive as a catalyzer.

Unquestionably many of the effects ascribed to *catalysis* are in reality due to the effectiveness of the heating by conduction and convection close to the surfaces of the refractory materials. The importance of *radiant energy* in causing hydrocarbon reactions has also been overemphasized most consistently in the literature of the gas industry. Too little attention has been paid to the *methods of making temperature measurements*, and also to the interpretation of temperature measurements made in certain ways. Thus it is obvious that a metal pyrod with a metal casing or a protective sheath of solid material such as quartz will absorb many times as much radiant energy as the gases in the heated space, and therefore indicate a temperature considerably above the true temperature of the gases. Also the conduction of heat along the metal pyrod casing is more effective than the conduction through a gas.

The processes of conduction and convection are

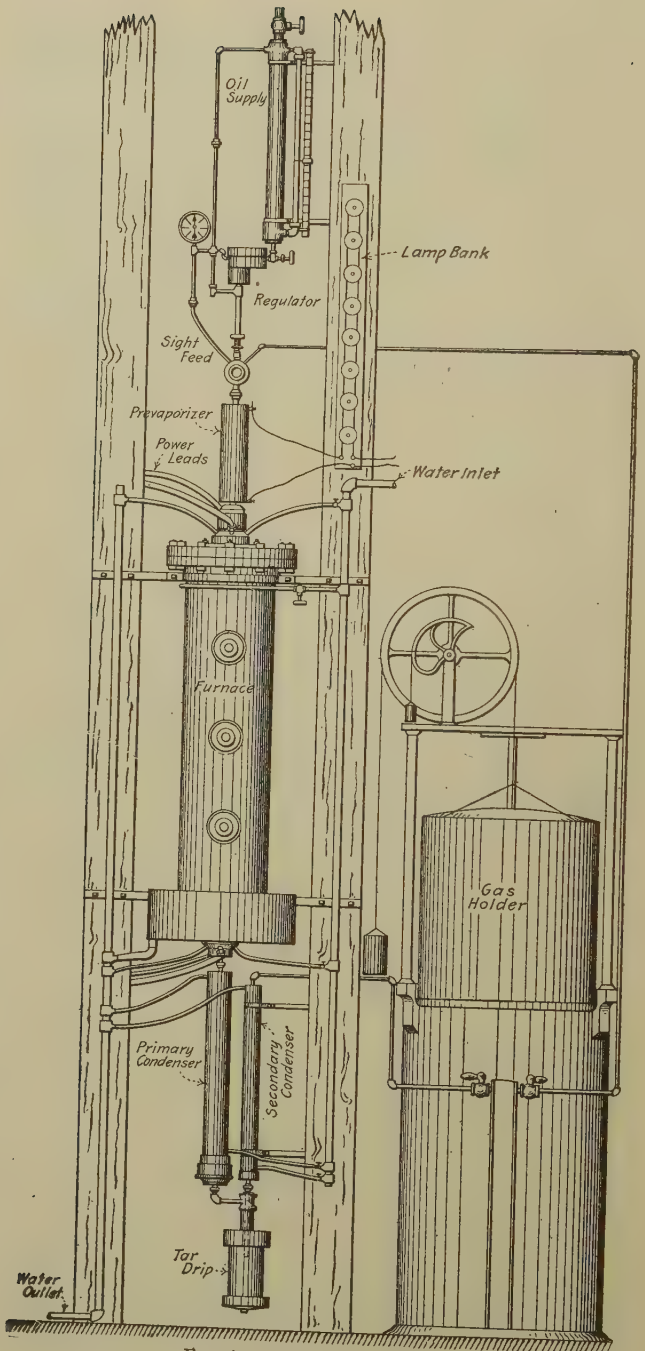


FIG. 1—OIL GAS APPARATUS

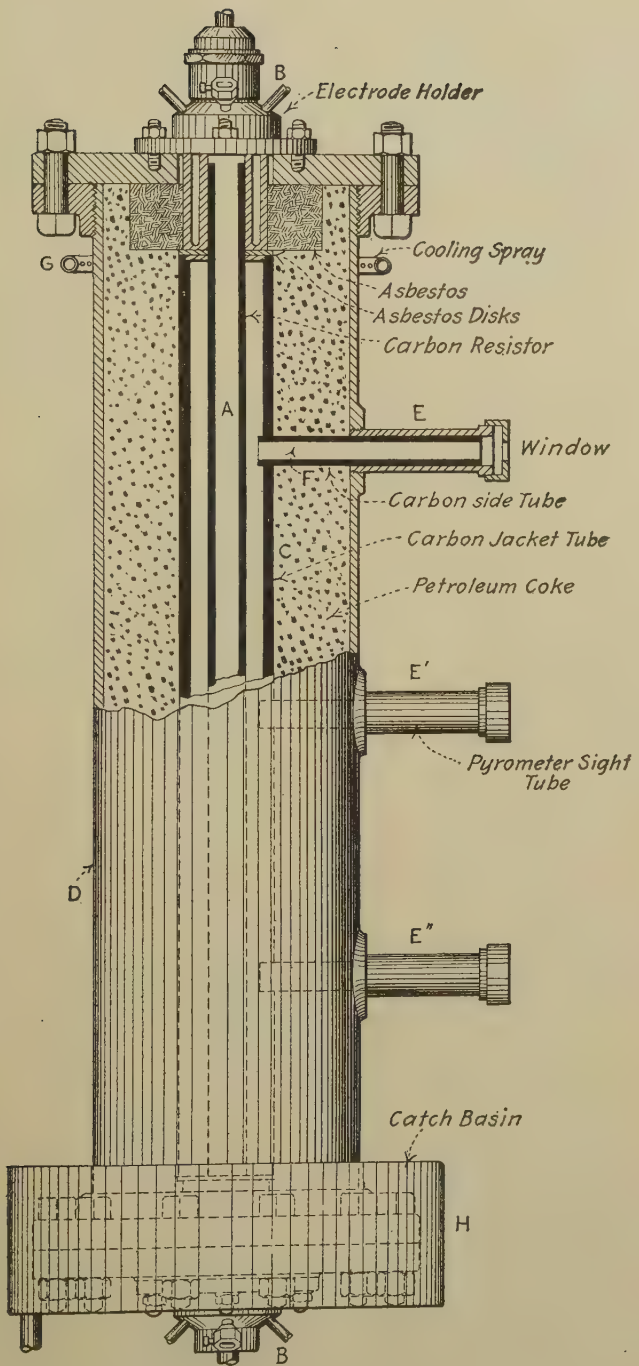


FIG. 2—RESISTANCE FURNACE

dependent on the extent of the heated surfaces exposed to the gas, and the manner in which the gases are made to pass over these surfaces. The heat transfer from the hot walls of the retort or checker-brick is primarily a matter of heat conduction through a thin layer of gas next to the hot surfaces, and second-

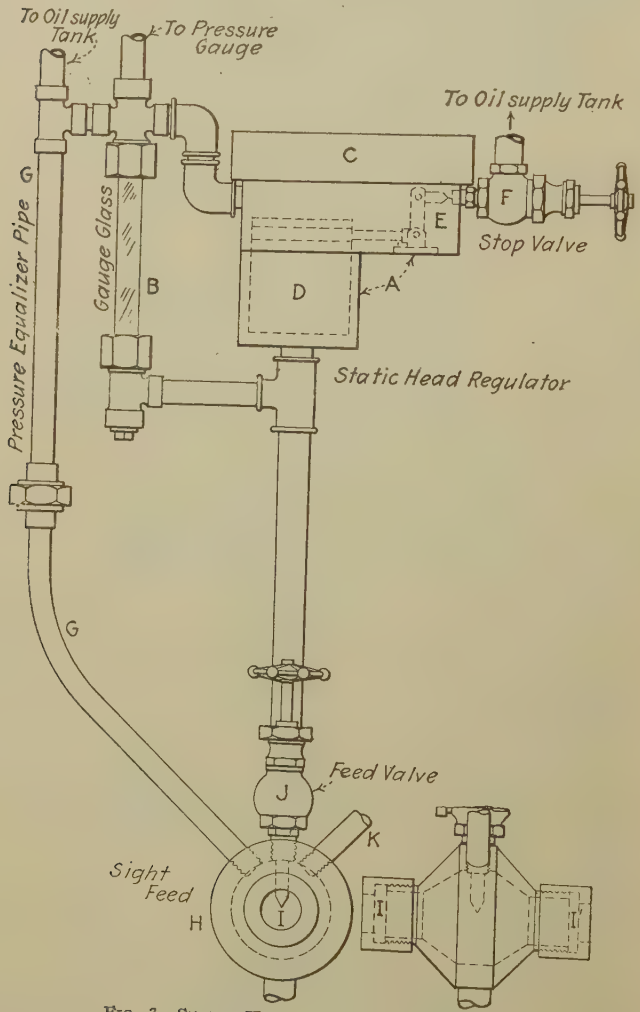


FIG. 3—STATIC HEAD AND FEED REGULATOR

arily a process of convection. Conceived of in terms of the kinetic molecular hypothesis, the molecules of the gas very close to the hot surfaces can be thought of as striking the surfaces, and in so doing having their kinetic molecular energy increased; then they dive out again into the surface layer of the gas where

by numerous impacts the newly acquired energy is given up to numbers of other molecules. The molecules from the main gas stream are constantly entering the surface layer and those in the surface layer are at all times entering the gas stream.

In addition to the increase in the kinetic energy of the molecules on account of their contact with the heated bricks, a chemical effect must no doubt be taken into account. Langmuir[1] has explained the abnormal heat losses from lamp filaments glowing in hydrogen on the assumption that the molecules

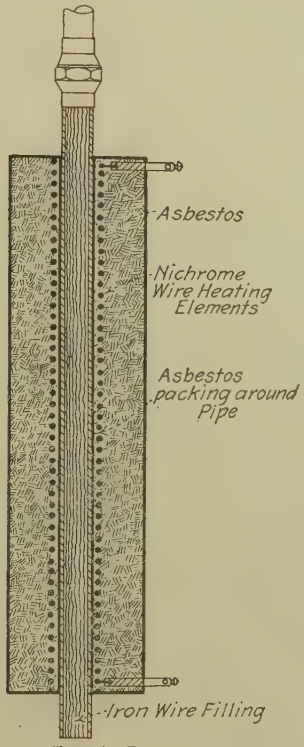


FIG. 4—PREVAPORIZER

of the gas dissociate into atoms with absorption of heat near the filament, and that the atoms then diffuse away from the wire and recombine with liberation of the heat at first absorbed.

Magnanini and Malagnini[2] have shown that the dissociation of a gas causes an abnormally high heat conductivity. They found that partially dissociated nitrogen tetroxide had three times as great a heat

[1] *Proc. Am. Electrochem. Soc.*, **20** (1911), 225–242.

[2] *Nuovo Cim.*, **6** (1892), 352.

conductivity as the completely dissociated gas. This idea can readily be applied to the transfer of heat in gas machines, for in them there exists a complex gaseous hydrocarbon system in which numerous endothermic reactions are possible in the highly heated layer close to the checkerbrick or retort surfaces. The products of these dissociations then diffuse into the outer layers, and recombine with liberation of the heat previously absorbed, thus effecting the heat transfer.

Lewes[1] cites experiments by Euchene showing that the temperatures of the gas above the coal in a retort varied from 700° C. 1/2 hour after charging to 950° C., 4 hours after charging; 9 in. of space were left above the coal in the retort and the flue temperature was approximately 1100° C. On p. 144 Lewes states that in a horizontal retort, with 1100° C. flue temperature, the gases left the mouthpiece at 400° C. during the first few hours of the period of carbonization and then dropped 100° C. during the last 2 hours. These statements appear as conflicting. It is hard to see why the temperature in the mouthpiece of the retort should not vary somewhat with the temperature of the gases in the retort. Further, it is difficult to believe that gases at 700° to 950° C. could be cooled to 400° C. in the mouthpiece. The temperature as observed in the mouthpiece is probably more nearly the true temperature of the gases in that part of the apparatus than the temperatures noted in the gas space above the coal in the retort are for the gases filling that space.

In the measurement of gas temperatures with a metal pyrod it is impossible to avoid the absorption of radiations from the solid bodies in the immediate vicinity. This would no doubt play an important part in the case at hand. The temperatures recorded by Euchene are in all probability too high on account of the absorption of radiant energy by the pyrod, whereas this energy is very incompletely absorbed by the gases. This difficulty would not be so marked at 400° C. because the emission of radiations of this type is proportional to the fourth power of the absolute temperature. Hence it seems not improbable that the temperatures for the gas above the coal in the retort as recorded are too high. However, if the gases were efficiently absorbing the radiations

[1] "Carbonization of Coal," pp. 132–133.

emitted by the hot walls of the retort, the temperatures of these gases would be at least as high as those recorded by him. Our inference is that this radiant energy is not absorbed to a large extent by the gases, and that conduction and convection play far more important parts in the heat transfer than radiation.

An excellent paper by Langmuir[1] discusses from a theoretical and practical point of view the heat transfer by means of radiation, conduction and convection from surfaces of various shapes into air. It is interesting to note that the air near a hot metal disk was heated to a point hot enough to char paper for a distance of only 1/4 in. from the disk even when the latter was heated to redness.

Thus in the superheater and carbureter the size of the voids between the checkerbricks must be very important in connection with the results to be obtained by the use of a certain temperature.

Tyndall and Magnus have both worked on the diathermacy of gases and vapors.[2] The following tables show some of the results of these investigators.

THE WORK OF TYNDALL—In these experiments the radiation from the heat source passed through a column of gas 33 in. long, and then upon a thermopile used to measure the radiant energy passing through the gas. The source of the radiant energy was a copper plate heated by a small impinging flame from a Bunsen burner.

EXPERIMENTS AT ATMOSPHERIC PRESSURE

SUBSTANCE	% Absorption of Radiations	SUBSTANCE	% Absorption of Radiations
Oxygen	0.08	Hydrogen sulfide	31.0
Nitrogen	0.08	Methane	32.0
Hydrogen	0.08	Amylene vapor	60.3
Carbon monoxide	7.1	Ethylene	71.0
Carbon dioxide	7.1	Ammonia	94.5
Benzol vapor	21.2		

The effect of pressure is shown by the following data:

SUBSTANCE	PER CENT ABSORPTION 0.1 Atm.	0.5 Atm.	1.0 Atm.
Benzene	5.25	14.5	21.2
Amylene	13.2	39.2	60.3

Thus the absorption increases with the pressure, but not in direct proportion to it, nor in accordance with any simple law.

The effect of temperature of the source of the radiant energy can be seen in the following data: The figures are not per cents of absorption but simply numbers

[1] *Proc. Am. Electrochem. Soc.*, **23** (1913), 299–332.

[2] Preston's "Theory of Heat," p. 551–568.

representing the relative absorptions as found in this particular set of experiments.

Substance	Barely Visible Red	Bright Red	White Heat
Benzene	26.3	20.6	16.5
Amylene	35.8	27.5	22.7

Thus the higher the temperature the less the absorption of radiant energy by these gases.

MAGNUS' EXPERIMENTS—The source of the radiant energy in Magnus' experiments was at the temperature of boiling water, and the distance through the gas traversed by the radiations was 15 in.

Substance	% Absorption	Substance	% Absorption
Vacuum	0.00	Methane	27.79
Oxygen	11.12	Cyanogen	27.79
Hydrogen	14.21	Ethylene	53.71
Carbon dioxide	19.77	Ammonia	61.12
Carbon monoxide	20.99		

These results are considerably lower than those obtained by Tyndall in the case of the hydrocarbon gases and ammonia, but higher in the cases of oxygen, hydrogen, carbon dioxide, and carbon monoxide. The high results with these last-mentioned gases seem to be due to the influence of convection and conduction in Magnus' experiments.

Langmuir has shown that out of a total heat loss of 0.670 watt per sq. cm. for a vertical oxidized silver plate 0.134 watt was radiated, and 0.536 watt were conduction and convection losses. The measurements were made in still air.

Although the radiation loss would be greater for a body under black body conditions such as exist approximately in retorts and gas machines the conduction and convection losses would be also greatly in creased by the rapid passage of the gases. Although no data are available on this question it seems a fair assumption that 25 per cent of the heat loss from any particular checkerbrick is radiated energy, while the rest of the heat is transferred by conduction and convection. As can be seen from the data of Tyndall and Magnus cited above, ethylene absorbs more radiant energy than any of the other gases listed except ammonia—the absorption lying between 55 and 77 per cent of all the available radiations. But this is for ethylene at 1 atmosphere pressure, while the partial pressure of ethylene in a water gas machine at no time exceeds 0.2 atmosphere. Also the measurements of Magnus and Tyndall were made at comparatively low temperatures whereas the temperature in the gas machine is in the neighborhood of 700° C.

The absorption of radiations by gases falls off with diminishing pressure, and also with increasing temperature. Taking these factors into consideration it is probable that not more than one-quarter of the available radiation is absorbed by the ethylene. On this basis only one-sixteenth of the total heat transfer from the checkerbricks to the ethylene is due to absorption of radiant energy. In the cases of the other gases it is less than this. For hydrogen it is almost negligible, and for carbon monoxide very small. Although molecular decomposition would not be expected in the cases of these gases at these temperatures, the fact that they are not effectively athermic is of importance; for did they absorb radiations to a large extent they would then transfer the heat so gained by molecular collision to the hydrocarbon molecules which are undergoing important molecular changes, and thus influence the course of the reactions.

In general then, it would seem that radiation does not play as important a part in transferring heat as has been taken for granted. Conduction and convection are largely responsible for this transfer, and they are helped to some extent by the dissociation reactions of the hydrocarbons. Catalysis has been greatly overrated. The influence on reaction rates supposedly brought about in this fashion can be better understood if the true mechanism of heat transfer is kept in mind. The different results of experimental investigations are also often easily understood if the shape and size of the apparatus is considered in its relation to heat transfer.

THE DECOMPOSITION OF HYDROCARBONS AND THE INFLUENCE OF HYDROGEN IN CARBURETED WATER GAS MANUFACTURE

II—EXPERIMENTAL

Although numerous studies of hydrocarbon decomposition have been made, no one, nor all combined, comprise a complete investigation.

The recent work[1] done in connection with the commercial production of gasoline and aromatic hydrocarbons has been the most exhaustive ever attempted. However, these investigations have not been carried out from the standpoint of gas production.

It is scarcely necessary to discuss the importance of a thorough understanding of the possibilities of controlling the decomposition of hydrocarbons for the obtaining of the particular products desired.

The most profitable utilization of an oil is of extreme importance to the water gas manufacturer. The control of the cracking of an oil is the thing of first importance to the manufacturer of oil gas in any of the various processes. The effect of the presence of hydrogen on the products derived from an oil is of great importance to the water gas manufacturer and the all-oil-water-gas maker.

Also it is generally recognized that the carbonization of coal and the combustion of coal and oil are allied problems, and that the results of a study of hydrocarbon decomposition are of direct application in these connections. The effect of the introduction of hydrogen into the carbonizing retorts can also be seen by a study of the data given in this paper.

Brief mention of the experimental work of a few investigators will serve to show the importance of the subject of hydrocarbon decomposition to the users of coal for gas making purposes or as a fuel.

Jones and Wheeler[2] have extracted solid paraffins from several British coals by means of pyridine and chloroform. Pictet and Ramseyer[3] have isolated hexahydrofluorene from that portion of a gas coal which was soluble in benzene. The same hydrocarbon

[1] Whitaker and associates at Columbia University, and Rittman and associates, U. S. Bureau of Mines.

[2] *J. Chem. Soc.*, **103** (1913), 1704.

[3] *Ber.*, **44** (1911), 2486; *Gas World*, **56** (1911), 131.

has been identified by them in the tar obtained by the low temperature distillation of coal in a vacuum. Burgess and Wheeler[1] found that paraffin hydrocarbons were predominant among the primary decomposition products of coal. The same authors[2] found a considerable evolution of higher olefins when coal was distilled at low temperatures. E. Bornstein[3] discussed the decomposition of coal at temperatures up to 450° C. He found that the gaseous products consisted of 5 to 14 per cent heavy hydrocarbons, 55 to 76 per cent paraffins, and 5 to 16 per cent hydrogen. Jones and Wheeler[4] distilled coals at temperatures up to 450° C. in a vacuum of 5 to 40 mm. of mercury, and obtained 6.5 per cent by weight of a tar which consisted of 25 per cent olefin hydrocarbons and an equal proportion of naphthenes and paraffins. Pictet and Bouvier[5] have conducted experiments similar to those of Jones and Wheeler, and found a large proportion of hydroaromatic or naphthene hydrocarbons in the tars. Porter and Taylor[6] found that the primary decomposition products of coal were complex easily liquefiable paraffins, hydrocarbons with smaller amounts of water, carbon dioxide and hydrogen.

One of the points in the propaganda of the various recently developed low temperature carbonization schemes has been the high percentage of light hydrocarbon oils which might be recovered from the tars and used for motor spirit. The gases obtained in these processes are also rich in higher hydrocarbons. Lewes[7] gives the analysis of a gas which contained 10.1 per cent of the members of the paraffin series higher than methane.

White, Park, and Dunkerley[8] found the ethane content of the gases of low temperature carbonization processes to run from 11 per cent to 47 per cent. Parr and Olin[9] have found that approximately 10 per cent of a light hydrocarbon oil was obtained from tars made in low temperature carbonization experiments between 400 and 500° C.

[1] *J. Chem. Soc.*, **99** (1911), 649–667.
[2] *Ibid.*, **105** (1914), 131–140.
[3] *Z. angew. Chem.*, **17** (1904), 1520.
[4] *J. Chem. Soc.*, **105** (1914), 140–151, 2562–2565.
[5] *Compt. rend.*, **157** (1913), 779.
[6] *Proc. Am. Gas Inst.*, **1914**, 234–288.
[7] "Carbonization of Coal," p. 164.
[8] *Proc. Michigan Gas Assoc.*, **17** (1908), 83.
[9] "Coking of Coal at Low Temperatures," *Bull.* **79**, Univ. of Illinois Experiment Station, 1915.

PURPOSE OF THE PRESENT INVESTIGATION

It is the purpose of this investigation in general to show what results may be expected in the decomposition of an oil if temperature, rate of oil feed, and concentration of hydrogen are taken into account and carefully controlled. More specifically it is proposed to show:

1—The variation of the composition of the gases made from oil at constant temperature and pressure with changing rate of oil feed.

2—The effect of changing the temperature on the composition of gases made from oil alone at constant oil feed and constant pressure.

3—The variation in the volume of the various gases obtained per cc. of oil fed at constant temperature and pressure but with changing rate of oil feed.

4—The effect of changing temperature on the volume of various gases obtained per cc. of oil at constant rate of oil feed and constant pressure.

5—The extent to which hydrogen is absorbed at any particular concentration, and the effect of changing the concentration.

6—The influence of hydrogen of certain concentration on the number of cc. of the various gaseous components obtained per cc. of oil, and the relations between this and change of concentration of hydrogen, change of temperature, and change of oil rate.

7—The results of a study of the mean molecular weight of the olefins in the gases at certain temperature, and the influence of the presence of hydrogen and change of the rate of oil feed in this connection.

8—The proportion of aromatic hydrocarbons present in the gases and the influence of the presence of hydrogen and changing oil rate in this connection.

9—The percentages of tar formed at different temperatures and rates of oil feed, and the influence of hydrogen on tar formation.

PLAN AND SCOPE OF THE EXPERIMENTAL WORK

The plan of the present work was to study the decomposition of paraffin hydrocarbons under atmospheric pressure, and at a number of temperatures and varying oil rate; and under identical conditions, to investigate the effect of the presence of hydrogen of different concentrations on the decompositions of the paraffin hydrocarbons.

The working temperatures were 621° C., 723° C. and 825° C. The temperatures used in the commercial

manufacture of water gas lie between 700 and 775° C., and are thus well within the temperature range of these experiments. At 927° C. two runs were made, but the separation of carbon in the furnace tube was so rapid it was impossible to keep the tube open while the adjustments for the hydrogen-oil gas runs were made. The hydrogen concentrations are discussed under the caption "The Hydrogen Concentration."

The method used was to adjust the furnace to the proper conditions and to run the oil in at the desired rate. The oil gas so made was collected. Without stopping the flow of oil, hydrogen was then admitted in proper concentration and the gas produced by cracking the oil in hydrogen collected in a second gasometer. The two gases were thus made under identical furnace conditions. The volumes of the tars formed were measured.

The straight oil gas runs made in connection with this research were a repetition of those previously made by Dr. C. M. Alexander (private communication); the results of whose work have not as yet been published. The experimental data of the work recorded here are in excellent agreement with those of Dr. Alexander.

APPARATUS AND PROCEDURE

THE FURNACE used in these experiments was designed and built by Whitaker and Alexander, and used by them in a study of the time factor in the making of oil gas.[1] For a detailed description of the furnace construction reference must be had to the original article.

The heating was effected by the passage of an alternating current from a single phase, 60 cycle, 50 kilowatt generator. The current passed through the carbon resistor tube of the furnace was readily controlled by means of a field rheostat. Thus a very accurate regulation of the temperature was obtained. Fluctuation limits of 1 or 2° C. were attained by careful operation.

A constant feed of oil was readily maintained by means of the static head and feed regulator. The oil was vaporized in the prevaporizer. The hydrogen gas was introduced into the sight feed just below the oil feed valve where it mixed with the oil vapors coming from the prevaporizer, and passed on into the heated tube of the furnace. The gas velocity in the tube could be calculated from its dimensions (1 in. I. D. × 38.5 in. long), and the total gas rate.

[1] *J. Ind. Eng. Chem.*, **7** (1915), 484–495.

Certain features of the design of the furnace, other than the fact that it was susceptible to exact control, which made it particularly suitable for the study of the reactions of hydrocarbon decomposition both from a theoretical standpoint and from an operating standpoint, must be pointed out. It is evident that the gas in passing through the carbon tube is subjected to a set of conditions similar to those existent in the interior of the water gas carbureter and superheater; *i. e.*, heated by carbon-coated passageway walls. Though the size of the furnace tube is less than the voids in the checkerbricking in the gas machine, the general conditions are the same.

Both from a theoretical standpoint and practical standpoint the study of the kinetics of these various hydrocarbon reactions is greatly to be desired as has been pointed out elsewhere in this paper. The furnace was designed in such manner as to avoid catalytic effects as completely as possible, and is therefore suitable for a study of the kinetics of such reactions.

MEASUREMENT OF GAS VOLUMES—The gases from the runs were collected in 5-cu. ft. holders. The dimensions of these tanks were carefully taken and the volumes computed. A stationary millimeter scale was attached to the tank standard, and a rigid pointer to the movable bell so that readings could be taken at given time intervals, and the gas rates and total volumes calculated.

A wet meter was used for the measurement of the volume and rate of the hydrogen flowing into the machine. This meter was filled with kerosene to avoid the aspiration of water vapor into the furnace. The oil level in the meter was adjusted carefully at all times, and the meter kept perfectly level. The meter was calibrated against the tank which was used for the collection of the mixed oil-hydrogen gases. The hydrogen was allowed to flow into the meter, through the furnace heated to 800° C. and into the receiving tank, readings being taken, at short intervals, of the meter rate and tank rate. This calibration was checked from time to time and found not to vary appreciably.

THE PYROD AND ITS CALIBRATION—The temperature measurements were made with a base metal thermocouple attached to a direct reading Wilson-Maeulen instrument. The thermocouple was calibrated by checking it against the boiling point of sulfur (444.6° C.) and against the melting point of sodium chloride (800° C.). The readings of the thermocouple at these

points were 425 and 775° C., respectively. Using these data a curve was plotted from which the true temperature could be read corresponding to temperatures as read from the instrument.

The temperatures at which runs were made were those observed when the pyrod projected through a suitable stuffing box into the lowest of the sight tubes. A hole the size of the end of the pyrod was made in the carbon resistor tube, and the pyrod allowed to project about $^1/_2$ in. into the interior of the resistor tube. The upper portion of the resistor tube was about 25–30° C. colder than that part of the tube where the pyrod was inserted, due, no doubt, to the cooling effect of the incoming gases and to the endothermic reactions taking place in that part of the tube.

THE HYDROGEN used in these experiments was a very high-grade electrolytic gas. Analyses showed it to contain 99.9 to 100.0 per cent hydrogen.

THE OIL used was a water-white oil (0.8000 sp. gr.), which boiled between 150 and 265° C.

METHOD OF OPERATION—The furnace was first heated up well and the jacket cooling water adjusted properly. When a constant temperature 10 to 30° above the temperature at which the run was to be made had been established, the oil valve was opened and adjusted to the proper rate of flow. The temperature of the furnace was then regulated till it remained constant at the desired point. The gases formed during this preliminary operation were run to a waste tank, and the tar discarded.

As soon as all the proper operating conditions had been established, the gases were run into a gas holder and readings of the oil rate, gas rate and temperature were taken at suitable short intervals. The pressure was always atmospheric. The temperature was noted at frequent intervals, and any necessary regulations of the field rheostat were made.

When the proper amount of gas had been collected, the gas was again sent to the waste gas holder, and the tar removed from the tar drip. Hydrogen was then admitted, flowing from the compressed hydrogen tank through the reducing valve and meter and into the admixer at the top of the furnace tube. When the rate of the hydrogen flow and all the other conditions had been adjusted, the gas passing was run into a second gas holder. Readings of the oil rate, hydrogen rate, total gas rate, and temperature were again taken at suitable intervals.

Thus an oil gas and a hydrogen-oil gas were made under exactly the same operating conditions. These gases were analyzed 18 to 20 hrs. after making. Analyses were made on low temperature, fast oil rate, gases at periods of one to two hours after making to see if the standing for longer periods caused any difference in the analytical results. No appreciable difference was found.

RELATION BETWEEN THE EXPERIMENTAL APPARATUS AND THE COMMERCIAL APPLIANCE

Frequently it is a difficult matter to reproduce experimental results in technical operation. It is with the object of calling attention to salient points which must be kept in mind in order that the results recorded here may be reproduced in a commercial appliance that the paragraphs which follow are written.

Experimental results show that the time factor is all important. But it must be remembered that the furnace tube used in these experiments was only 30 in. long, whereas the column of checkerbrick in the carbureter and superheater of the water gas set is many times that length. Hence even though a pyrometer may record the same temperature in this furnace and in the checkerbrick of a commercial machine it would not be expected that the gases would have the same composition.

The diameter of the furnace tube used in these experiments was 1 in. This, however, was soon carbonized so that it was more nearly $^3/_4$ in. The interstices in the checkering of commercial machines are of greater sectional area than a circle of $^3/_4$ in. diameter. Hence the opportunity for heat transfer in the checkerbrick is not so good as in this experimental furnace and it would be expected that a longer column of checkerbrick than was necessary in this furnace would be necessary to produce a given result, all conditions being the same.

The actual time of contact of the gases with heated surfaces is all important, but it is a very complicated function of the rate of oil feed, the amount of blue gas introduced, the volume of the checkerbrick voids, and the temperature.

Commercial operation demands that an apparatus have a reasonable gas making capacity, and for this reason the higher oil rates are most desirable. On the other hand, with high oil rates more tar is always produced than at low oil rates, which makes the use of

the oil uneconomical. It is not improbable that the best results could be obtained by designing one apparatus with proper control suitable to the production of certain gaseous products, and a second apparatus which would use the tar from this first machine as the carbureting oil. An examination of the tars formed in the experimental apparatus at medium to high rates of oil feed have led to the belief that this would not be impracticable.

Methods of temperature measurement must not be neglected. Above all it must not be assumed that a particular temperature as measured will produce the same results in two different machines.

The experiments recorded in this paper merely show the possibilities in the decomposition of a hydrocarbon oil. To obtain particular results on a commercial scale would necessitate a great deal of thought as to the proper design for the machine to be used.

THE HYDROGEN CONCENTRATION

The introduction of hydrogen in certain concentration is a question which must be regarded from at least two standpoints; *i. e.*, the experimental and the technical or operating standpoints.

In the manufacture of carbureted water gas the oil is cracked in an atmosphere of carbon monoxide and hydrogen. The final gas is roughly $^1/_3$ hydrocarbons, $^1/_3$ hydrogen and $^1/_3$ carbon monoxide. The hydrogen and hydrocarbons are thus present in the approximate ratio of 1 volume to 1 volume in the final gas. In addition there is present 1 volume of carbon monoxide, the influence of which has never been exactly determined by a comprehensive study.

In these experiments it was thought desirable to study two concentrations of hydrogen:

(1)— 1 Volume Hydrogen : 2 Volumes (oil gas + tar gas)
(2)— 2 Volumes Hydrogen : 1 Volume (oil gas + tar gas)

The experimental difficulties were such, however, that the introduction of hydrogen in exactly these proportions was practically impossible, for, with change in temperature, the amount of gas produced from a given quantity of oil at a particular rate changes, while with change in oil rate at constant temperature the amount of gas produced from a given quantity of oil changes. Also the gas formed from a certain amount of oil is different when the oil is decomposed alone or in an atmosphere of hydrogen. Furthermore, the concentration of hydrogen in the upper part of the

furnace tube is much greater at any time than it is in the lower part of the tube, for as the oil vapors pass through the tube a progressive decomposition takes place with formation of a greater volume of hydrocarbon gases.

It would therefore be necessary to make several trial runs at each oil rate at each temperature to determine the proper hydrogen rate. When it is considered that each run of that sort would consume several hours' time, the impracticability of this method of procedure is apparent. Furthermore, in commercial operation the two factors which would be susceptible to control would be the rate of introduction of blue gas and the rate of introduction of the oil. So it was decided to base the hydrogen concentration arbitrarily on the oil rate. After some trials at 723° C., the following equations relating to the hydrogen rate and the oil rate were decided upon:

(1) To approximate 1 Vol. Hydrogen : 2 Vols. (oil gas + tar gas)

$$\frac{\text{Oil rate in cc. per minute}}{5.28} = \left\{ \begin{array}{l} \text{Hydrogen rate in liters} \\ \text{per minute.} \end{array} \right.$$

(2) To approximate 2 Vols. Hydrogen : 1 Vol. (oil gas + tar gas)

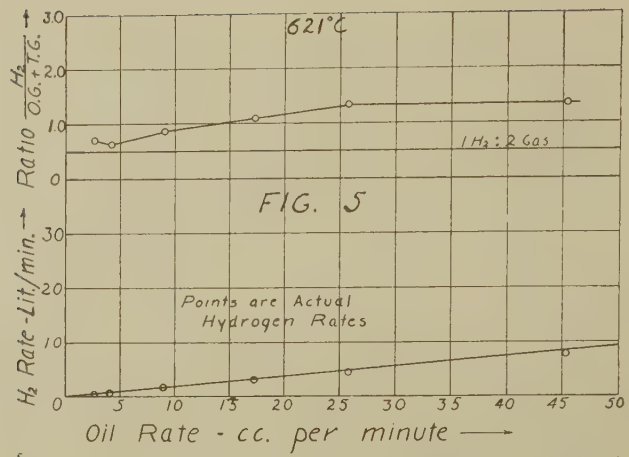
$$\frac{\text{Oil rate in cc. per minute}}{1.76} = \left\{ \begin{array}{l} \text{Hydrogen rate in liters} \\ \text{per minute.} \end{array} \right.$$

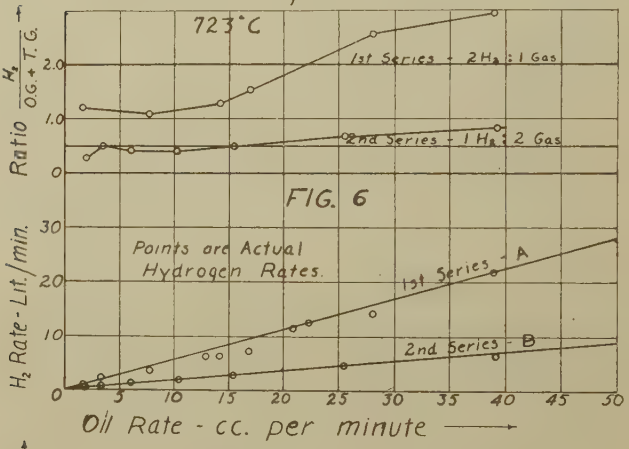
One set of runs only was made at 621° C. and this at the supposed ratio *1 Vol. Hydrogen : 2 Vols. Gas.* The lower curve in Fig. 5 is plotted from the equation given under (1) above. The points represent the actual hydrogen rates and show how closely it was possible to adjust the hydrogen rate to that desired as calculated from the oil rate.

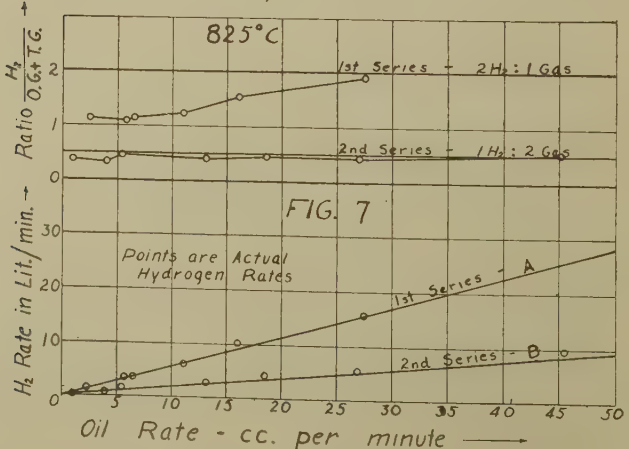
The upper curve in Fig. 5 shows the actual ratio of hydrogen to (oil gas + tar gas). In the furnace the hydrocarbons which compose the tar are of course gaseous and the volume of this gas is calculated on the assumption that the specific gravities of the liquid tars are 0.80 (water = 1) and that the mean molecular weight of the hydrocarbons contained in the tar is 142; *i. e.*, that the average molecule contains 10 carbon atoms.

The straight line at ordinate 0.5 is the theoretical curve for the value of the ratio of hydrogen to (oil gas + tar gas). It can be seen that the value of this ratio more nearly approximated unity than it did 0.5 in these runs.

A second series of runs with the value 2 for the ratio of hydrogen to (oil gas + tar gas), was not made for







EFFECT OF DIFFERENT HYDROGEN CONCENTRATIONS WITH VARYING OIL RATES AT THREE TEMPERATURES
Data for Curves Calculated on Two Bases

the reason that from the results at higher temperatures it was judged that the chief effect of more hydrogen at 621° C. would be to blow the vapors through the heated tube faster without producing extensive chemical change. Since there was approximately 1 volume of hydrogen to 1 volume of (oil gas + tar gas), in these runs at 621° C., that is, practically the relations existent in the carbureter and superheater of the water gas set, it was thought that this series of runs sufficed to show the possibilities of a temperature in the neighborhood of 621° C. for purposes of gas manufacture.

Curves A in Figs. 6 and 7 are the plots of the equation under (2) given above at 723 and 825° C., respectively, and curves B in Figs. 6 and 7 the plots of equation (1) above at those temperatures. The points show how closely the actual hydrogen rates approximated those calculated by these equations.

The lower curve in the upper half of Fig. 6 shows that the actual value of the ratio of hydrogen to (oil gas + tar gas) approximated very closely to the value 0.5 drawn horizontally on the ordinate 0.5. The upper curve in the upper half of Fig. 6 shows that at low oil rates too little hydrogen was introduced to make the value of the ratio hydrogen to (oil gas + tar gas) equal to 2.0, and at high oil rates that too much hydrogen was introduced.

The actual values of the ratio hydrogen to (oil gas + tar gas) in the second series of runs at 825° C. are shown in the curves in the upper half of Fig. 7. In the first series of runs the value of the ratio lies between 1.0 and 2.0, whereas it was intended that it should be 2.0. In the second series the desired value 0.5 is very closely approximated at all oil rates.

ANALYTICAL PROCEDURE FOR GASES

During the early part of the work recorded in this paper the method of gas analysis was the ordinary one employing the Hempel burette with single and double pipettes for the absorbing reagents. Thus the carbon dioxide was removed by a solution of 1 part of KOH in 2 parts of water, the unsaturated and aromatic hydrocarbons by fuming sulfuric acid with 20 per cent free SO_3, the oxygen by alkaline pyrogallol made up in accordance with Hempel's directions,[1] and the carbon monoxide absorption in ammoniacal cuprous chloride prepared according to Winkler.[2] A portion of the residual gas was then mixed

[1] Dennis' "Gas Analysis," p. 160.

[2] C. Winkler, "Handbook Tech. Gas Anal.," translated by Lunge, p. 73.

with oxygen, and slowly passed back and forth over palladium black in a glass tube immersed in water at a temperature of about 85–90° C. After thus removing the hydrogen the gas mixture was exploded over mercury, and the resulting carbon dioxide absorbed in potassium hydroxide.

"CARBON MONOXIDE"—As the work progressed it became evident that this method could be improved upon. It was difficult to understand where the carbon monoxide, varying from 0.2 per cent to 1.9 per cent as shown by the cuprous chloride absorption, could have come from. The furnace was tight, and in any case there would be a slight positive pressure outwards, so that the ingress of air in more than small amounts was out of the question. The only other possible source of oxygen was the water in the oil used. However, had the carbon monoxide arisen thus from the reaction of steam on the carbon it would have been present in larger amount at 800° C. than at 600° C. Also there should have been some relation between the percentages of carbon monoxide and carbon dioxide. But carbon monoxide, as indicated by the absorption in ammoniacal cuprous chloride, was present in largest amount at 600° C., in smaller amounts at 700° C., and least of all at 800° C. Also it was noticed that at any particular temperature the carbon monoxide tended to be highest when the oil rate was highest. However, there was no regular variation of this sort as there was with the other components of the gaseous mixtures formed. Hence it appeared that the "carbon monoxide" formation as shown by the absorption in the ammoniacal cuprous chloride was not solely a function of the furnace conditions.

F. C. Phillips[1] stated that cuprous chloride solution dissolved the higher members of the paraffin series to some extent. G. A. Burrell and F. M. Seibert[2] found that cuprous chloride solution caused a contraction of 0.5 to 0.6 per cent in Pittsburgh natural gas. They have also shown that a two-minute contact of cuprous chloride solution with pure ethane caused a loss in volume of 0.6 per cent and that in five minutes the contraction was 1.4 per cent.

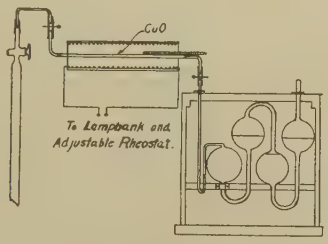
Our experimental work showed that those gases which would be expected to have the largest proportion of high molecular weight hydrocarbons, *i. e.*, those

[1] "Oil and Gas Levels," W. Va. Geol. Survey, **1A** (1904), 552.

[2] "The Sampling and Analysis of Mine and Natural Gases," Bur. of Mines, *Bull.* **42**, 46–77.

gases made at low temperatures and fast rates of oil feed, were also those which showed the highest percentages of "carbon monoxide." It appeared certain, therefore, that the contractions found on passing the gases into the ammoniacal cuprous chloride solution were in reality largely due to absorption of paraffin hydrocarbons such as ethane, propane, and butane rather than to carbon monoxide.

The use of ammoniacal cuprous chloride was therefore abandoned, and the carbon monoxide and hydrogen determined by Jaeger's fractional combustion method somewhat as described by H. C. Porter and G. B. Taylor.[1] In place of the vertical Nichrome resistance heater with the inverted U-tube to hold the copper oxide, a horizontal heater with a straight copper oxide tube was used as shown in the accompanying drawing.



Apparatus for Fractional Combustion of CO and H_2 over CuO

The difference in temperature between the bottom and top of the vertical heater was great enough so that when the oxide was at the proper temperature in one part of the containing tube, it was either too hot or too cold in other parts of the tube. With the horizontal heater and the copper oxide tube running concentrically through it no such difficulty was experienced, nor did the water formed during the combustion cause any trouble.

The fractional combustion of gaseous mixtures over copper oxide consumes a little more time with gases which are low in hydrogen and high in paraffins than does the method in which the cuprous chloride pipettes and the palladium black are used. However, as the average time for carefully made analyses is not over 45 mins., this cannot be considered as a serious disadvantage.

It was found that a temperature of 275–280° C. burned the carbon monoxide and hydrogen to carbon dioxide and water without affecting the methane

[1] *Proc. Am. Gas Inst.*, **9** (1914), 255; *J. Ind. Eng. Chem.*, **6** (1914), 845–8.

and other paraffin hydrocarbons present. After passing the gases over the oxide till no further contraction took place, they were allowed to cool to room temperature, and the volume read. The contraction at this point equals the per cent of hydrogen in the gas. The carbon dioxide was then absorbed in potassium hydroxide. This contraction is equal to the per cent of carbon monoxide in the gas. The importance of allowing the gases to reach room temperature can readily be seen. Otherwise the contact with the potassium hydroxide will cause a contraction due to the lowering of the temperature of the gas.

The method of burning the carbon monoxide and hydrogen over copper oxide has recently been discussed by G. A. Burrell and G. G. Oberfell.[1] Their experiences with this method were apparently similar to ours.

In the case of many of the gases obtained in the experimental work, the gas residue after the fractional combustion was small enough so that the whole of it could be mixed with oxygen and exploded over mercury. Here again the method of burning over copper oxide presents a distinct advantage over the methods first mentioned above, for in the combustion with palladium black it is necessary to mix the gas with oxygen previous to the fractional combustion of the hydrogen. Thus a much smaller proportion of the gas could be put through the partial combustion and explosion analysis, in consequence of which accuracy was sacrificed. Accuracy at this point was particularly desired in order to calculate the mean molecular weight of the paraffins.

AROMATIC HYDROCARBONS—At the outset of this work the desirability of determining the extent of the formation of hydrocarbons of the benzene series was evident. A careful survey of the literature, however, showed that none of the methods proposed had given satisfaction in the hands of all who had worked with them. It was not until the work recorded here was nearing completion that the method proposed by Hulett and developed by the Bureau of Mines[2] came to our attention. This method was used for the determination of the aromatics in the gases from one series of runs at 825° C.

[1] *J. Ind. Eng. Chem.*, **8** (1916), 228–231.

[2] G. A. Burrell, F. M. Seibert, and I. W. Robertson, "Analysis of Natural Gas and Illuminating Gas by Fractional Distillation at Low Temperatures and Pressures," *Technical Paper*, **104**, 26–27.

The procedure in brief is to evacuate the apparatus with a good pump, after which the gas is admitted and the temperature and barometer readings noted. The gas is allowed to stand for some time (in these determinations 2 to 3 hrs.), in order that the phosphorus pentoxide may remove the water vapor completely, and then immersed for 10 to 15 mins. in a mush of carbon dioxide snow in acetone contained in a Dewar flask. At the end of this time the gases are sucked off by means of the pump. The bulbs are then removed from the cold bath and allowed to come to room temperature. The temperature is noted and the partial pressure of the volatilized aromatics is read on the short arm manometer. From this data the volumetric percentage of these components in the gas can be calculated. A rotary oil pump which gave a vacuum of less than 1 mm. of mercury, and that in less than a minute, was used in these experiments.

MEAN MOLECULAR WEIGHT OF THE OLEFINS

When the analysis and the specific gravity of a gas are known the mean molecular weight of the heavy hydrocarbons of the gas can be calculated. When, in addition to the percentages of carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen, the percentage of aromatics is known, the mean molecular weight of the olefins and acetylenes can be calculated.

In determining the specific gravity the temperature of the gas and the barometer reading should be taken, and the gas should be thoroughly shaken with water in order to saturate it with water vapor at the temperature of the room before introducing it into the specific gravity apparatus. Time should be allowed for the subsidence of any mist formed during the agitation with water.

The method used for the determination of the specific gravity was the so-called effusion method and the apparatus was similar to that described by Pannertz.[1] The orifice was made by pricking a piece of thin platinum foil with a needle, and then beating the foil with a small leather mallet till the tiny hole was visible only when held up to a strong light. This foil was mounted on the end of a short brass tube fitting with a carefully turned brass screw cap luted in with litharge and glycerol cement.

Certain errors are inherent in the experimental methods used. In the first place it is well known that

[1] *J. für Gasbel*, **48** (1905), 901.

fuming sulfuric acid absorbs higher paraffins during the determination of the heavy hydrocarbons.[1] It was thought that the use of bromine water might obviate this difficulty, but analyses on 621° C. gases made by both methods checked to within 0.1 per cent showing that the two reagents were having similar effects. F. C. Phillips[2] says that bromine water absorbs the higher paraffins.

Disagreement between analyses made by the use of bromine water and by fuming sulfuric acid may be occasioned by the fact that bromine water does not brominate benzene. In the analyses made in these experiments there is little doubt but that the benzene would have been completely scrubbed down on account of the time and shaking necessary to obtain complete reaction between the olefins and the bromine solution. Also the proportion of benzene present in a 621° C. gas made at atmospheric pressure is not large.

The absorption of higher paraffins by the fuming sulfuric acid can be avoided in large part by the use of small portions of the reagent in an apparatus of the type described by G. B. Taylor.[3] It was thought, however, that the time required for analyses made in this way would be too great.

Another error inherent in the method of determining the mean molecular weight of the olefins lies in the fact that the method for aromatics does not differentiate between benzene, toluene, or xylene. An average molecular weight must be assumed here which evidently is not absolutely correct. In the calculations all aromatics have been regarded as if they were benzene, since it was believed that this hydrocarbon comprised the greatest portion of the aromatics present in the gas.

A further error lies in the fact that the paraffins were all assumed to be methane and ethane. Higher homologs of this series are without doubt present as has been shown by Burrell, Seibert, and Robertson in their analyses of carbureted water gas and coal gas by the method of fractional distillation at low temperatures.[4]

A certain proportion of naphthenes or polymethylenes are also no doubt present among the products of the pyrogenic decomposition of the hydrocarbons of

[1] R. P. Anderson and J. C. Engelder, *J. Ind. Eng. Chem.*, **6** (1914), 989–92; R. A. Worstall, *J. A. C. S.*, **21** (1899), 245; Orndorff and Young, *Am. Chem. J.*, **15** (1893), 249; Burrell and Seibert, "Sampling and Analysis of Mine and Natural Gas," Bur. of Mines, *Bull.* **42** (1913), 45–47.

[2] "Oil and Gas Levels," W. Va. Geol. Survey, **1A** (1904), 522.

[3] *J. Ind. Eng. Chem.*, **6** (1914), 845.

[4] Bureau of Mines, *Tech. Paper*, **104** (1915); *J. Ind. Eng. Chem.*, **7** (1915), 17–21.

kerosene. To what extent these are affected by the fuming sulfuric acid, and to what extent they are carried through the analysis and credited to the paraffins cannot be stated. Data on the exact behavior of the cyclobutanes, cyclopentanes, and cyclohexanes when treated with fuming sulfuric acid have not been found, if, in fact, such information is at all available.

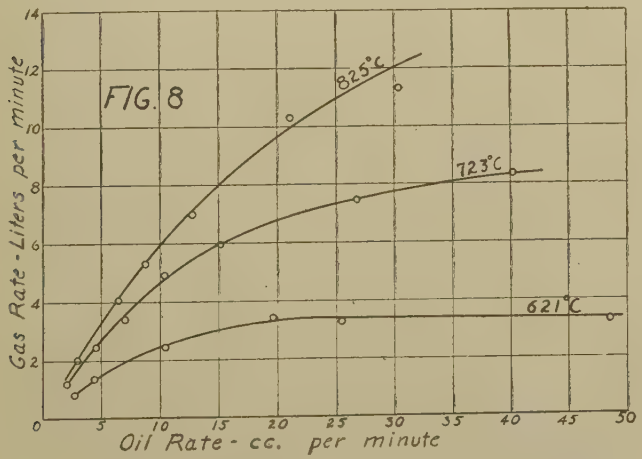
In addition to the errors already mentioned is the experimental error in the determination of the specific gravity by the effusion method. Check determinations were always made on the time of flow, and it was found possible to get agreements to within less than 0.5 per cent.

The following analyses are cited to compare the results obtained by the usual procedure with Hempel burette and pipettes with those obtained by the use of the various modifications discussed above. These will be designated for the sake of brevity as the "Standard" method and the "CuO" method, respectively.

	Gas No. 24		Gas No. 24		Gas No. 25	
Method:	Standard	CuO	Standard	CuO	Standard	CuO
Carbon dioxide.....	0.3	0.0	0.1	0.1	0.0	0.0
Heavy hydrocarbons...	48.1	48.2	47.9	49.8	49.3	50.8	50.7
Oxygen.....	0.5	0.5	0.5	0.5	0.5	0.4	0.4
Carbon monoxide.....	1.2	0.2	0.2	0.9	0.1	1.1	0.1
Hydrogen.....	11.9	11.9	12.1	9.3	9.2	10.4	10.3
Paraffins.....	37.3	37.6	37.7	38.1	38.4	37.0	37.2
Total.....	99.3	98.4	98.5	98.7	97.6	99.7	98.7

THE GAS RATE

The gas rates for three temperatures are plotted against the oil rates in Fig. 8. At 621° C. the gas rate



Variation of Gas Rate with Various Oil Rates at Three Temperatures

increases with the oil rate up to an oil rate of 20 cc. per minute, but the introduction of more oil per minute causes no further increase in the gas rate. Apparently

with a heated tube of the dimensions used here only a certain quantity of oil can be affected in a given time by heat at a temperature of 621° C. A similar limitation would be expected in a commercial machine operating at this temperature. At 723° C. the gas rate is greater with greater oil rate at all oil rates studied. Judging from the shape of the curve and from the analogy of the 621° C. curve it is apparent that an increase in oil rate above 45 to 50 cc. per minute would produce no increase in the gas rate. At 825° C. the gas rate increases with increase in oil rate as can be seen, and at the oil rates studied there is no apparent tendency for a rate to be reached beyond which there is no further increase. Obviously, however, such a point would be reached.

In comparing the gas rate curves it is interesting to note that at low oil rates the change in temperature from 621 to 723° C. has a much greater effect than the change from 723 to 825° C. At low oil rates a temperature of 723° C. is sufficient to gasify permanently the greatest portion of the oil. The slightly greater production of gas at 825° C. is largely due to the decomposition of methane into carbon and hydrogen.

As the oil rate increases, a temperature of 723° C. becomes less and less effective for the purpose of permanently gasifying the oil; 825° C. is much more effective, as can be seen from the increasing divergence between the curves.

THE DECOMPOSITION OF PARAFFIN HYDROCARBONS

Figs. 9 to 14 indicate the proportions of the various components obtained when the oil was decomposed alone. Fig. 9 shows that at 621° C. the gases are composed of about 10 per cent hydrogen at all oil rates above 5 cc. per minute. The reactions which contribute to the formation of this hydrogen, named in order of their probable importance, are:

$$(1)\quad C_2H_6 \rightleftharpoons C_2H_4 + H_2$$
$$(2)\quad C_2H_4 \rightleftharpoons C_2H_2 + H_2$$
$$(3)\quad CH_4 \longrightarrow C + 2H_2$$
$$(4)\quad C_2H_2 \longrightarrow 2C + H_2$$

The conditions are those which are known to be favorable to the condensation of acetylene. The methods for the determination of acetylene are so unsatisfactory that no effort was made to determine the proportion of acetylene in the gases formed. Other investigators have found the amount small in similar experiments.

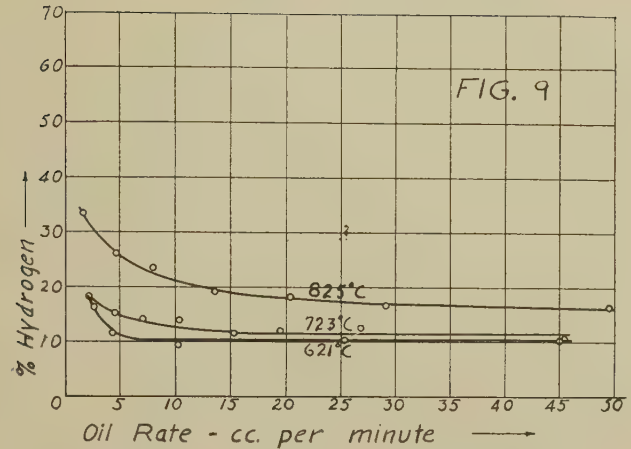


FIG. 9
% Hydrogen
825°C
723°C
621°C
Oil Rate - cc. per minute

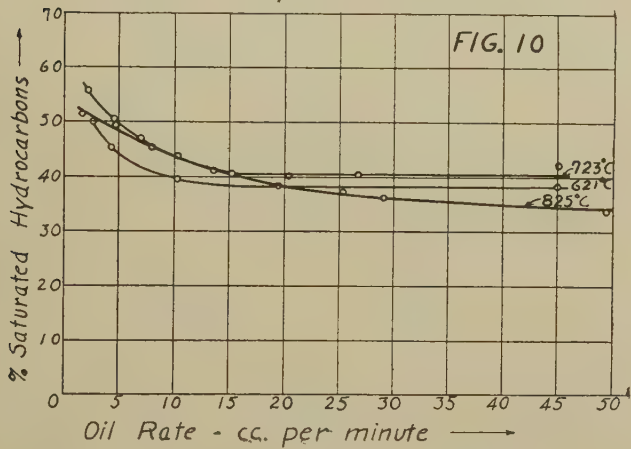


FIG. 10
% Saturated Hydrocarbons
723°C
621°C
825°C
Oil Rate - cc. per minute

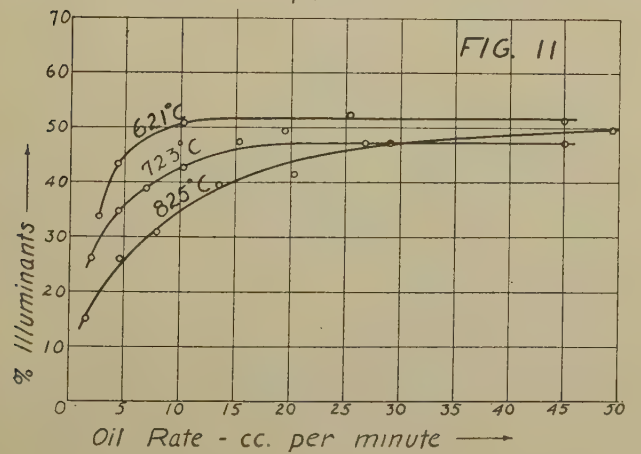


FIG. 11
% Illuminants
621°C
723°C
825°C
Oil Rate - cc. per minute

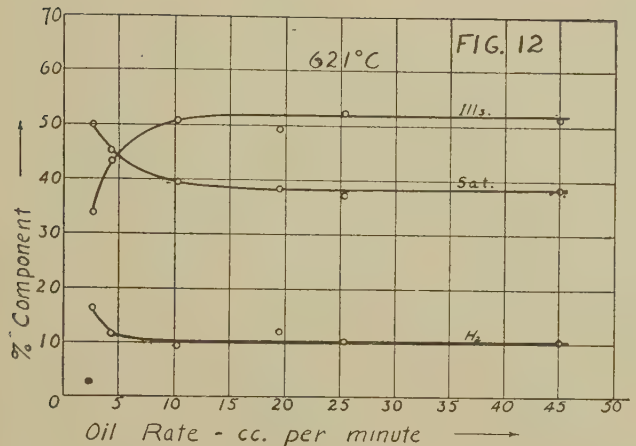
The rapid increase in the proportion of hydrogen with decreasing oil rates below 5 cc. per minute is thought to be due to a marked increase in the extent to which reactions (*3*) and (*4*) take place. At 723° C. only a slightly larger proportion of hydrogen is formed than at 621° C., indicating that reactions (*3*) and (*4*) do not become rapid up to this temperature. A very marked increase in the hydrogen production takes place when the temperature is elevated to 825° C., chiefly due to an increase in reactions (*3*) and (*4*), as is evidenced by the very large amount of free carbon which was liberated and which tended to stop the furnace tube. No trouble was occasioned by this carbon deposition at 621° C. or 723° C.

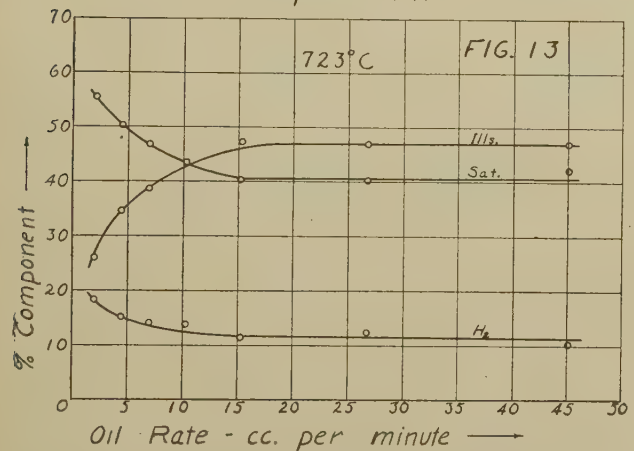
Fig. 11 shows the proportion of illuminants, or components removed by 20 per cent fuming sulfuric acid, in the oil gases made at the three temperatures. The percentage of illuminants is highest in the gases made at 621° C. at all oil rates, and remains practically constant at 52 per cent at all oil rates above 10 cc. per minute. The proportion of illuminants formed at 723° C. is higher than at 825° C. except possibly at high oil rates. It is thought, however, that the proportion of illuminants at high oil rates would not be greatly different at any of these temperatures.

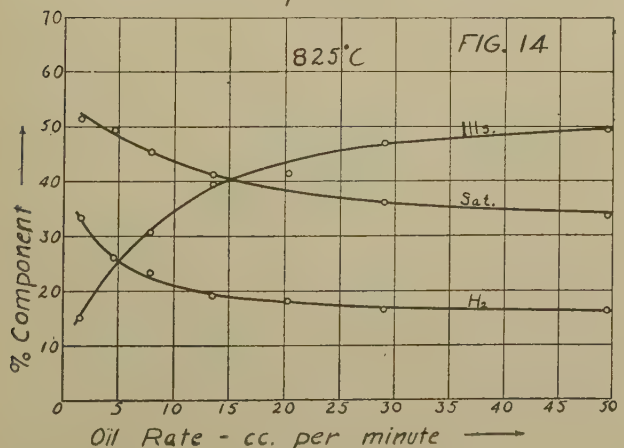
The fact that the proportion of illuminants is lower, the higher the temperature at moderate to low oil rates is due to the secondary reactions of these hydrocarbons. Ethylene is decomposed into carbon and methane to some extent. Condensation to naphthenes takes place. At these low oil rates the proportion of hydrogen present is considerable, and the higher the temperature the higher this percentage. Hence it would be expected that hydrogenation reactions such as $C_2H_4 + H_2 \rightleftarrows C_2H_6$ and $C_2H_4 + 2H_2 \rightleftarrows 2CH_4$ would take place.

The relation between the proportions of saturated hydrocarbons formed at different temperatures is shown in Fig. 10. It can be seen that the proportion of saturateds in the gas is higher at 723° C. than at 621° C. at all oil rates. This no doubt is due to the faster speeds of such reactions as $C_2H_4 \longrightarrow C + CH_4$ and $C_2H_6 + H_2 \rightleftarrows 2CH_4$.

It might reasonably be expected that the percentage of saturateds in the gases would be greater at 825° C. than at 723° C., but it can be seen from Fig. 10 that this is not the case. At low oil rates the proportion of saturateds is lower at 825° C. than at 723° C.


621°C
FIG. 12
IIIs.
Sat.
H2
% Component
Oil Rate - cc. per minute


723°C
FIG. 13
IIIs.
Sat.
H2
% Component
Oil Rate - cc. per minute


825°C
FIG. 14
IIIs.
Sat.
H2
% Component
Oil Rate - cc. per minute

This is chiefly due to the fact that the reaction $CH_4 \longrightarrow C + 2H_2$ has an appreciable velocity at this temperature. As the oil rate increases it would be reasonable to expect that the effect of this reaction would be less and less. However, the divergence between the 825° C. curve and the 723° C. curve becomes greater the faster the oil rate. This state of affairs is apparently due to the superimposed effect of another reaction. When the high paraffin hydrocarbons first break down under these conditions the chief products are low molecular weight paraffin hydrocarbons and high molecular weight olefins. At 621° C. and 723° C. a considerable proportion of the high molecular weight olefins formed pass on through the tube into the tar. The tars were larger in amount the lower the temperature, and when the tar curves are studied it will be seen that there is not a marked difference between the tar formation at 621° C. and 723° C. but that a considerable difference is found at 825° C. These low temperature tars were treated with concentrated sulfuric acid in the cold, and it was found that 20–25 per cent by volume was removable in this fashion, the greater portion of which was doubtless olefins of high molecular weight. At 825° C. the effect of the heat is sufficient to break down these higher olefins almost completely. In the process ethylene and propylene are formed in large quantity with the result that the percentage of saturated hydrocarbons drops. The proportion of illuminants and saturated hydrocarbons present in the gases at 825° C. is greatly lowered on account of the high percentage of hydrogen present in these gases.

Figs. 12, 13 and 14 show the relations between the component illuminants, saturateds, and hydrogen at the temperatures 621° C., 723° C. and 825° C., respectively. Of all the proportions of these components those at the high oil rates at 621° C. most nearly represent the products of the primary decomposition of the oil. The hydrogen is largely the result of secondary reactions. If the illuminants and saturateds are calculated to a 100 per cent basis the proportion is 58 per cent illuminants and 42 per cent saturateds. Such a ratio as this would be expected in the reaction if the primary decomposition of the paraffin was:

$$\underset{\text{Paraffin}}{C_nH_{2n+2}} \longrightarrow \underset{\text{Olefin}}{C_{n-1}H_{2n-2}} + CH_4$$

and, if then, the high molecular weight olefins in part broke down to lower olefins.

The mechanism of the reactions at work can be judged somewhat from a consideration of the relations between the curves for the percentages of illuminants, saturateds, and hydrogen. Thus, in Fig. 12, if it is assumed that the illuminants are chiefly ethylene and the saturateds largely methane it can be seen that the normal formation of ethylene is 52, that of methane 39, and that of hydrogen 10 per cent.

Consider the proportions in the gas at an oil rate of 2.5 cc. per minute. They are ethylene 34, methane 50, and hydrogen 16 per cent. The decrease in ethylene has been 18 per cent on the basis of the total gas. If this had been due to the reaction $C_2H_4 \longrightarrow C + CH_4$ the methane should have increased 18 per cent on the basis of the total gas. In fact it increases only 11 per cent.

The hydrogen increases 6 per cent on the total gas basis. If this were due to the reaction $CH_4 \longrightarrow C + 2H_2$ a 3 per cent decrease in the methane should have taken place. But as has been seen, other reactions also give rise to hydrogen. Assuming, however, that the above reaction was the sole change of this sort, only 14 per cent out of the 18 per cent increase in methane which should have been found, had the ethylene reacted entirely with formation of carbon and methane, would be accounted for. Hence the ethylene must be removed in other ways, for example by the condensation to naphthenes.

It is not probable that the 6 per cent increase in the hydrogen is entirely due to the decomposition of methane. Dehydrogenation of naphthenes, dissociation of ethylene and ethane, etc., may give rise to hydrogen. Then, too, not all the methane formed comes from the decomposition of ethylene. Decomposition of higher olefins in such a manner as

$$CH_3.CH_2.CH_2.CH{=}CH_2 \longrightarrow CH_4 + CH_2{=}CH{-}CH{=}CH_2$$

and hydrogenation of olefins, $C_2H_4 + 2H_2 \rightleftarrows 2CH_4$, may contribute.

A similar argument may be worked out for the relation between the illuminants, saturateds, and hydrogen at 723° C. and 825° C.

The marked decrease in illuminants with decreasing oil rates at 825° C. is notable. No corresponding increase in saturateds takes place. It is apparent

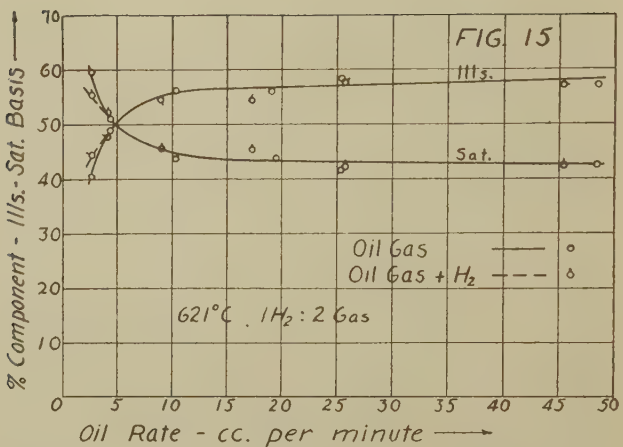


FIG. 15
% Component - Ills.-Sat. Basis
Ills.
Sat.
Oil Gas
Oil Gas + H_2
621°C 1 H_2 : 2 Gas
Oil Rate - cc. per minute

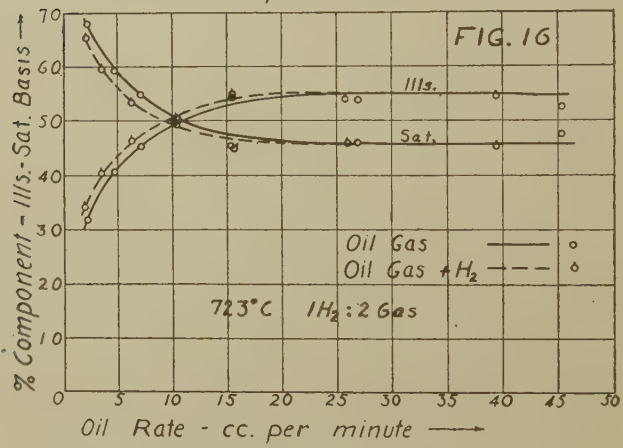


FIG. 16
% Component - Ills.-Sat. Basis
Ills.
Sat.
Oil Gas
Oil Gas + H_2
723°C 1 H_2 : 2 Gas
Oil Rate - cc. per minute

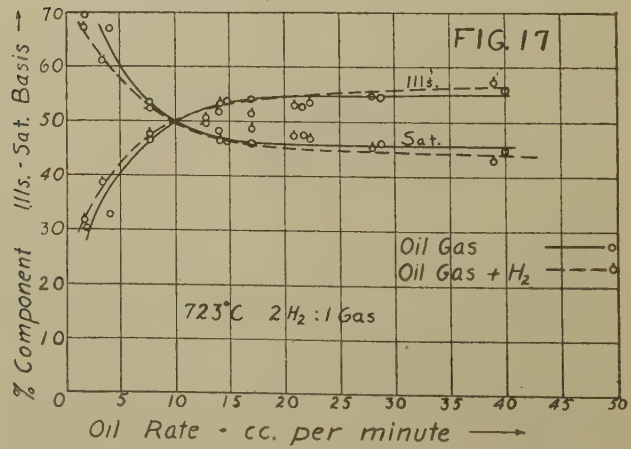


FIG. 17
% Component Ills.-Sat. Basis
Ills.
Sat.
Oil Gas
Oil Gas + H_2
723°C 2 H_2 : 1 Gas
Oil Rate - cc. per minute

from the high percentage of hydrogen that methane is decomposing extensively into carbon and hydrogen.

PROPORTION OF ILLUMINANTS AND SATURATED HYDROCARBONS

In order that the effect of hydrogen on the composition of the gases as regards illuminants and saturated hydrocarbons may be seen, Figs. 15, 16, 17, 18 and 19 are shown. These curves were drawn by calculating the illuminants and saturated hydrocarbons to a basis of 100 per cent. In this manner the proportions of the two classes of compounds can be seen.

It might be expected that hydrogenation reactions would play an important part and that the proportion of saturated hydrocarbons would be higher in the oil-gas-hydrogen runs than in the straight oil-gas runs. It will be shown later in this paper that hydrogenation does take place to a considerable extent.

It should be noticed that at low temperatures the presence of the hydrogen has no influence on the relative amounts of illuminants and saturated hydrocarbons at high oil rates; *i. e.*, its presence has little effect on the mechanism of the primary decomposition and the early stages of the secondary decomposition. But at low oil rates where the gases are exposed to the effect of heat for a longer time, and where extensive secondary and tertiary changes take place the hydrogen has a considerable influence at temperatures of 723° C. and 825° C. At 621° C. the influence of the hydrogen is not marked.

It will be remembered that the first reaction undergone by a paraffin hydrocarbon when it is thermally decomposed is that which gives rise to a high molecular weight olefin and a low molecular weight paraffin. It is probable that the higher the molecular weight of an olefin the more readily it is hydrogenated.

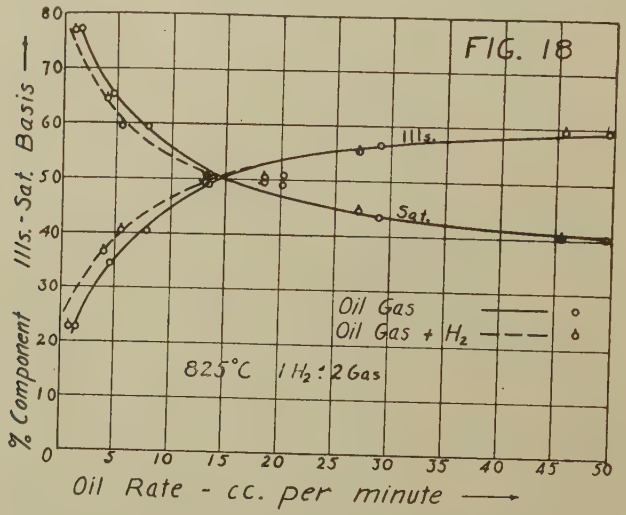
If the high molecular weight olefins are hydrogenated paraffins would be formed. These would again decompose into long chain olefins and low molecular weight paraffins. This sequence of reactions may be represented as follows:

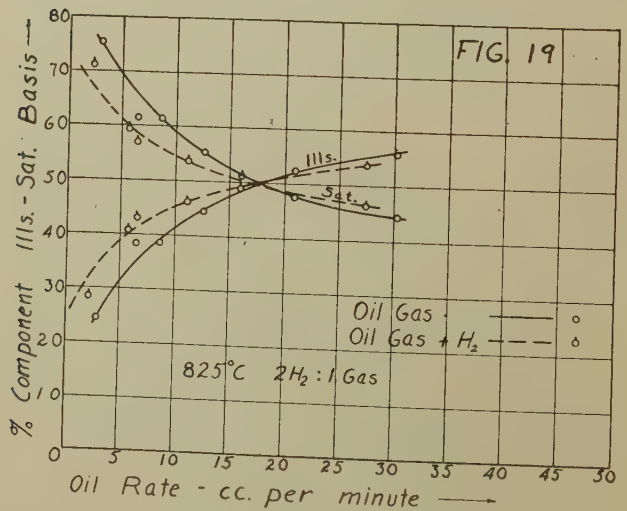
$$\underset{\text{Paraffin}}{C_nH_{2n+2}} \longrightarrow \underset{\text{Olefin}}{C_{n-1}H_{2n-2}} + CH_4$$

$$\underset{\text{Olefin}}{C_{n-1}H_{2n-2}} + H_2 \longrightarrow \underset{\text{Paraffin}}{C_{n-1}H_{2n}}$$

$$\underset{\text{Paraffin}}{C_{n-1}H_{2n}} \longrightarrow \underset{\text{Olefin}}{C_{n-2}H_{2n-4}} + CH_4$$

The net result of such a sequence of reactions would be an increase in the proportion of paraffins in the gas. But as can be seen in the figures, the proportion of paraffins is less in the cases of the hydrogen-oil gases. However, at high oil rates where secondary reactions are not so important, and in the series of runs at 825° C. where the concentration ratio was





2H2 : 1 gas (Figs. 17 and 19), the proportion of saturated hydrocarbons is greater in the hydrogen-oil-gas runs. It is probable, therefore, that the above reactions take place in all cases but that the effect of the hydrogen at low oil rates on the extensive secondary

changes is so great that the result of the hydrogenation is masked.

Apparently the low molecular weight olefins are not hydrogenated to a large extent, for were this the case the proportion of saturated hydrocarbons present would be greatly increased. This is not the case.

The increase in the proportion of olefins in the hydrogen-oil-gas runs at low rates of oil feed may be accounted for in two ways:

(1)—The effect of the hydrogen may be to increase those reactions which give rise to olefins.

(2)—The effect of the hydrogen may be to retard those reactions which tend to remove or destroy the olefins.

The largest proportion of the ethylene and propylene present comes from the direct splitting up of high molecular weight olefins. If an olefin of fairly high molecular weight may be used to illustrate, this reaction may be represented:

$CH_3CH_2CH_2CH{=}CH_2 \longrightarrow CH_3CH{=}CH_2 + CH_2{=}CH_2$

It will be noticed that the result is an increase in volume. The equilibrium point of the reaction would therefore be shifted by a diminution of pressure in such direction as to favor the production of ethylene and propylene. The introduction of hydrogen has the same effect as a reduction in pressure, and would therefore have a similar effect on the equilibrium.

Chief among the reactions which remove olefins such as ethylene and propylene are condensation and decomposition. These reactions may be represented as $3C_2H_4 \longrightarrow C_6H_{12}$ and $C_2H_4 \longrightarrow C + CH_4$.

The presence of the hydrogen would displace the equilibrium point of the first of these reactions in favor of the ethylene. The latter reaction, insofar as the influence of volume relationships on the equilibrium point is concerned, would not be affected.

Whether the displacement of the equilibrium points in any of these reactions is sufficient to be worthy of mention can not be said. In no case is the equilibrium condition attained, but the speeds of the various reactions would depend on the difference between the actual condition of the system and the equilibrium condition; hence any displacement of the equilibrium point would be important.

The increase in the proportion of olefins may be looked upon from another angle. When hydrogen is introduced along with the gas the time of contact of the gas with the heated tube is diminished, due to the

increase in the total volume passing in unit time. If it is the case that the reactions which give rise to the olefins ethylene and propylene are fairly rapid, while those which destroy them are slower, the summational effect of an increased gas rate would be an increased proportion of olefins. That the speed of the reactions which produce olefins is fairly great can be seen by reference to Fig. 22, which shows the mean molecular weight of the olefins formed at 825° C. The mean molecular weight lies between 30 and 34. The molecular weight of ethylene is 28, while that of propylene is 42. The proportion of olefins higher than propylene cannot be great, therefore, and it would seem that they break down largely to ethylene and propylene. That the reactions which cause a removal or destruction of ethylene are only moderate in speed has been seen under the discussion of the reactions of ethylene in the first part of this paper.

This latter explanation appears more probable than the one concerning the displacement of the equilibrium points of reactions; however, both of these effects may be concerned in the production of the results observed.

It will be noticed that the two different hydrogen concentrations produce similar results at 723° C. but that at 825° C. the proportion of olefins is much higher when the concentration ratio is $2H_2 : 1$ *Gas*. The rather large difference in this last case indicates that the chief effect of the hydrogen is due to its cutting down the time of heating, for at 825° C. the decomposition of the higher olefins to ethylene is doubtless very rapid, and takes place extensively in spite of the reduced time of heating in the hydrogen-oil gas runs.

THE ABSORPTION OF HYDROGEN

Calculations from the analytical data show that a considerable absorption of hydrogen takes place when the oil is cracked in an atmosphere of this gas. Haber was of the opinion that the oil produced no hydrogen by its own decomposition when it was cracked in an atmosphere of hydrogen. On the other hand, it might be assumed that there would be as much hydrogen produced under these conditions as when the oil was cracked alone. These two assumptions offer two bases on which the absorption of hydrogen may be calculated.

(1)—If no hydrogen is produced by the cracking of the oil, the hydrogen absorption per cc. of oil would

be equal to the difference between the hydrogen added and that present in the final gas divided by the total number of cc. of oil.

(2)—If the oil produces as much hydrogen as when cracked alone, the difference between the hydrogen added plus that normally produced from the oil at the particular oil rate and the hydrogen in the final gas represents the absorption. This divided by the total number of cc. of oil gives the absorption in cc. per cc. of oil.

Fig. 21 shows the absorption per cc. of oil calculated on basis (1) for the several temperatures and concentrations. Fig. 22 shows these absorptions calculated on basis (2).

It will be seen that the curves of Fig. 22 are much smoother and more regular than those of Fig. 21, not because they are drawn more smoothly, but because the points fall on smoother curves. The general form of the curves, too, in Fig. 22 is that which would be expected from a consideration of the curves for the hydrocarbon components formed per cc. of oil. The curves of Fig. 21 show no general similarity to each other, while those of Fig. 22 show similar general characteristics. The curves representing the formation of all the other components of the gases show regular variations, and it would be expected that this regularity would extend to the curves for hydrogen absorption.

In general, therefore, it seems that the basis on which the curves of Fig. 22 are calculated is more nearly correct than the basis which assumes that no hydrogen is produced from the oil when it is decomposed in hydrogen. This view is strengthened by the fact that in the case of the 825° C. gases with hydrogen concentrates *1H_2 : 2 Gas*, the absorption curve in Fig. 21 falls below the 0.0 line, *i. e.*, hydrogen must have been formed from the oil since there was more hydrogen in the final gas than was added through the meter.

It is probable that the true value for the hydrogen absorptions for any set of conditions falls between the two values as calculated from the two limiting assumptions. It is thought that the true values are slightly less than the values of the absorptions as they would be read from the curves in Fig. 22.

The curves of Fig. 22 show the interesting fact that at any particular temperature the hydrogen absorption per cc. of oil decreases with increasing oil rate. The

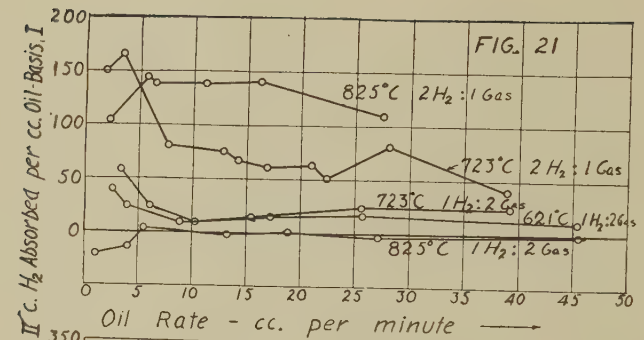


FIG. 21
825°C 2H2 : 1 Gas
723°C 2 H2 : 1 Gas
723°C 1H2:2Gas
621°C 1H2:2Gas
825°C 1H2 : 2 Gas
Cc. H2 Absorbed per cc. oil - Basis II C. H2 Absorbed per cc. Oil Basis I
Oil Rate - cc. per minute

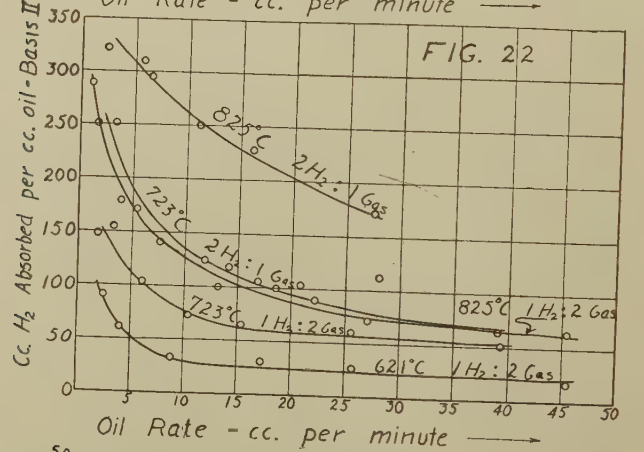
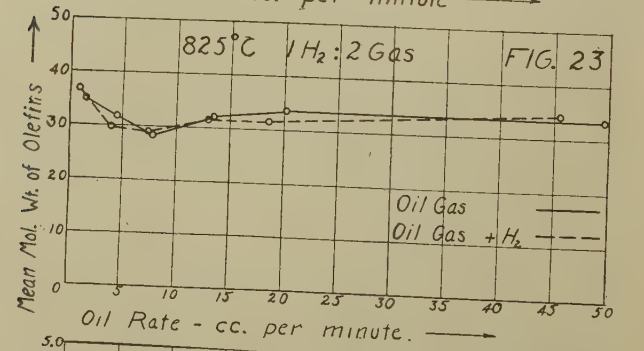
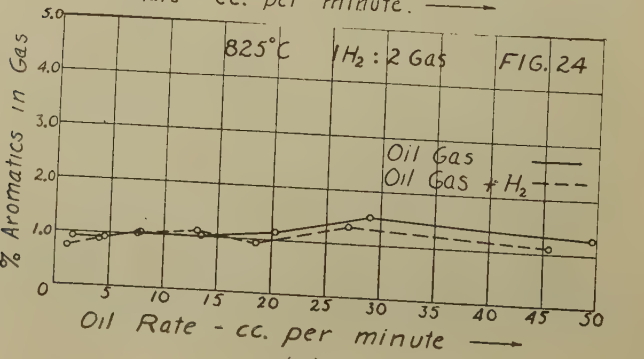


FIG. 22
825°C 2H2 : 1 Gas
723°C 2H2 : 1 Gas
723°C 1H2 : 2 Gas
825°C 1H2 : 2 Gas
621°C 1H2 : 2 Gas
Cc. H2 Absorbed per cc. oil - Basis II C. H2 Absorbed per cc. Oil Basis I
Oil Rate - cc. per minute


825°C 1H2 : 2 Gas
FIG. 23
Oil Gas
Oil Gas + H2
Mean Mol. Wt. of Olefins
Oil Rate - cc. per minute.


825°C 1H2 : 2 Gas
FIG. 24
Oil Gas
Oil Gas + H2
% Aromatics in Gas
Oil Rate - cc. per minute

great importance of the time factor is well brought out here. At constant oil rate, and approximately the same hydrogen concentration the absorption per cc. of oil is greater the higher the temperature. There would, however, be an upper limit to this on account of the excessive decomposition of all hydrocarbons at elevated temperatures.

The effect of increasing the concentration of hydrogen is clearly shown in Fig. 22, for the curve for the $2H_2 : 1$ *Gas* runs in above the curve for the $1H_2 : 2$ *Gas* runs at both 723° C. and 825° C. The speed of hydrogenation reactions is greater the higher the concentration of hydrogen.

It is interesting to note that the curve for the $1H_2 : 2$ *Gas* runs at 825° C. falls below the curve for the $2H_2 : 1$ *Gas* runs at 723° C. This shows that the increasing temperature is tending to cause dehydrogenation reactions or hydrocarbon dissociations to a marked degree at 825° C. The effect of hydrogen in greater concentration in reversing these dissociations is clearly brought out when the position of the $2H_2 : 1$ *Gas* curve for 825° C. is considered in its relation to the $1H_2 : 2$ *Gas* curve at this same temperature.

MEAN MOLECULAR WEIGHT OF THE OLEFINS

In Fig. 23 the mean molecular weight of the olefin hydrocarbons in gases made at 825° C. in oil-gas runs and in hydrogen-oil-gas runs with the concentration ratio $1H_2 : 2$ *Gas* can be seen.

It should be kept in mind that the molecular weight of ethylene is 28 and that of propylene is 42. From the position of the curves it can be seen that approximately one-third of the olefins is propylene. The curves lie very close together, and it is impossible to say just what the influence of the hydrogen is on the formation of the olefins.

If the method of calculation of the molecular weight of the olefins, as explained under the discussion of the analytical methods, is considered, it is apparent that all the analytical errors pile up and are brought out in this calculation. This no doubt accounts for the irregularity in the curve, and also for the fact that there is no consistent difference in the position for the oil-gas run and the hydrogen-oil-gas runs.

It was thought that certain differences might be brought to light by the curves for the mean molecular weights of the olefins. If the higher olefins were more easily hydrogenated than ethylene the curve for the

mean molecular weight of the olefins in the hydrogen-oil-gas runs would fall below that of the oil runs. If, on the other hand, the presence of the hydrogen, on account of its causing a more rapid passage of the gas through the tube, resulted in a less extensive decomposition of the higher olefins, the curve for the hydrogen-oil-gas runs would lie above that for the oil-gas runs.

It may be thought that these two effects are balancing each other with the result that the curves are practically the same. It would have been desirable to have carried out a similar series of runs with a high concentration of hydrogen, but the calculation of the mean molecular weight of the olefins can be made only when the per cent of benzene in the gas is known, and, as has been noted, the method for the determination of benzene was found only as this experimental work was drawing to a close.

THE FORMATION OF AROMATIC HYDROCARBONS

Fig. 24 shows the percentage of aromatic hydrocarbons present in the gases made at 825° C. when oil is cracked alone or in hydrogen when the concentration ratio is $1H_2 : 2$ (*Oil Gas* + *Tar Gas*). The method of determining these percentages has been described under the analytical methods.

The percentage of aromatics appears to increase slightly with increase in oil rate. Whether this is actually the case or not cannot be definitely stated. The exact opposite would be expected. It is thought that the apparent increase may be due to the freezing out of high molecular weight hydrocarbons of other types than the aromatic compounds. High molecular weight paraffins and olefins are present in greater proportion in the gases made at high oil rates than in those made at low oil rates.

The smaller proportion of aromatic hydrocarbons present in the gases made at low oil rates may possibly be due to the removal of benzene to form compounds such as diphenyl, naphthalene and anthracene, which pass largely into the tars.

The hydrogen apparently has little effect on the formation of aromatics at low oil rates, but decreases the aromatic formation somewhat at higher oil rates. This is possibly due to the retarding effect which the presence of hydrogen would have on the formation of aromatics or hydroaromatics by condensation reactions. Less gas is formed from the oil at high oil

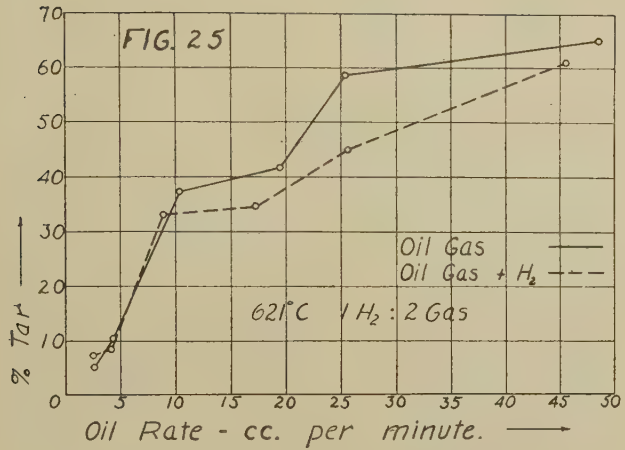


FIG. 25
% Tar
Oil Rate - cc. per minute.
Oil Gas
Oil Gas + H_2
621°C 1 H_2 : 2 Gas

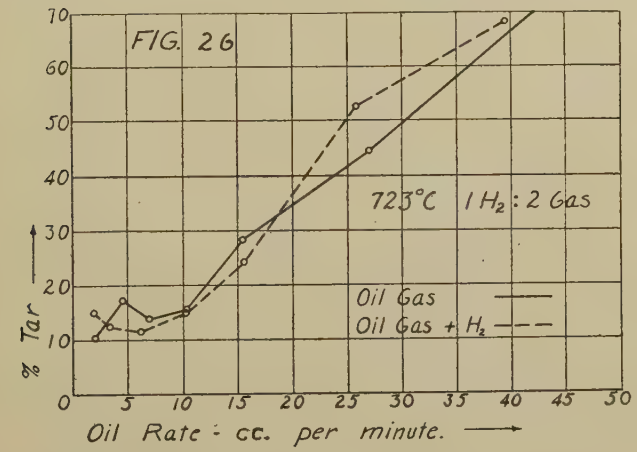


FIG. 26
% Tar
Oil Rate - cc. per minute.
723°C 1 H_2 : 2 Gas
Oil Gas
Oil Gas + H_2

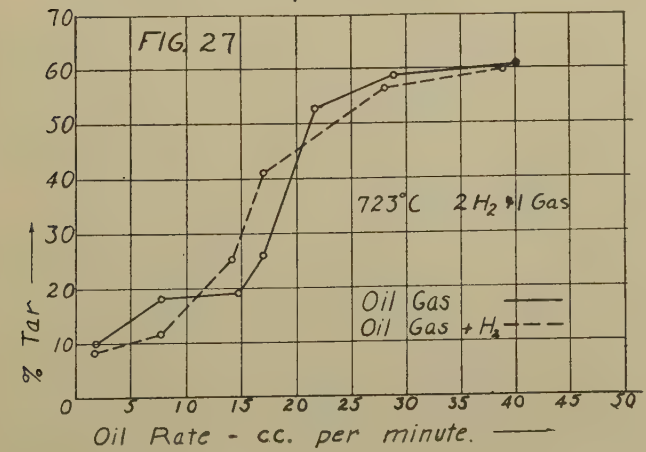


FIG. 27
% Tar
Oil Rate - cc. per minute.
723°C 2 H_2 : 1 Gas
Oil Gas
Oil Gas + H_2

rates than at low oil rates, and as a consequence the concentration of hydrogen is greater at high oil rates than at low oil rates.

TARS

The tars were collected from the tar drip and the volume measured. This volume divided by the volume of the total oil used and multiplied by 100 gives the percentages of tar formed. Figs. 25 to 29 show these tar percentages for both *oil-gas* and *hydrogen-oil-gas* runs plotted against the oil rate at the temperatures indicated. It should be mentioned that at low oil rates these percentages are not accurate. The low-oil-rate tars are heavy and viscous, and as a result do not run down through the condenser as easily as the lighter high-oil-rate tars.

As far as can be judged from the curves in Figs. 25, 26, and 27, for temperatures of 621° C. and 723° C. there is no marked regular difference between the tar formation in the oil-gas runs and the hydrogen-oil-gas runs.

At 825° C. the percentage of tar in the oil-hydrogen runs is consistently less than in the oil runs except at low oil rates where, as has been mentioned, the tar percentages as shown mean little. This difference is more marked in the curves of Fig. 26 where the concentration ratio was *2 Hydrogen : 1 (Oil Gas + Tar Gas)* than in the curves of Fig. 28.

In general two classes of compounds are contained in the tar: *first*, unchanged or partially changed oil; *second*, synthetic hydrocarbons which are the products of extensive change. It may be thought that hydrogen, on account of its decreasing the time of contact of the hydrocarbon vapors with the heated tube, would tend to increase the proportion of tar since the decrease in the time of heating would cause a less extensive decomposition of the oil vapors. On the other hand, this decrease in the time of heating would also diminish the extent to which synthetic reactions resulting in the formation of tarry products would take place. Also the percentages of the hydrogen would retard these reactions, since they are all reactions which result in decrease of volume. Apparently these effects are balanced at temperatures of 723° C. or below. At 825° C., however, the percentage of tar is less. This leads to the belief that synthetic reactions are responsible for a considerable proportion of the tars at temperatures in the neighborhood of 825° C.

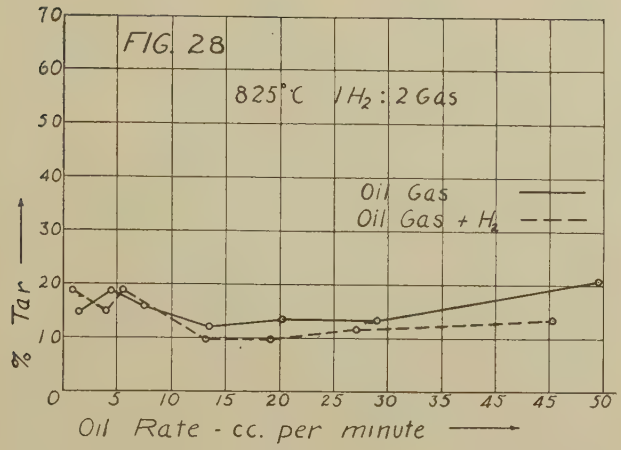


FIG. 28
825°C 1 H_2 : 2 Gas
Oil Gas
Oil Gas + H_2
% Tar
Oil Rate - cc. per minute

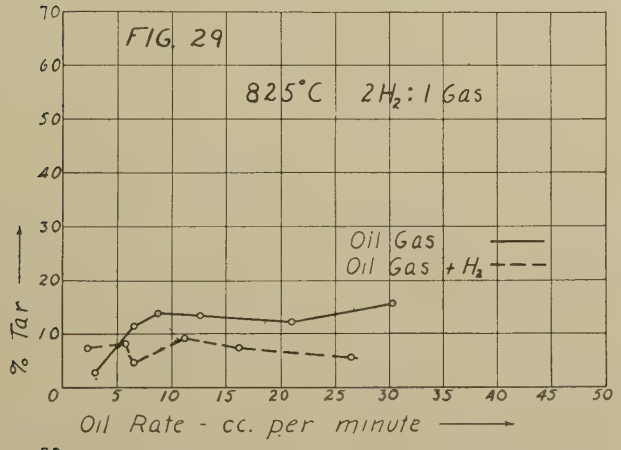


FIG. 29
825°C 2 H_2 : 1 Gas
Oil Gas
Oil Gas + H_2
% Tar
Oil Rate - cc. per minute

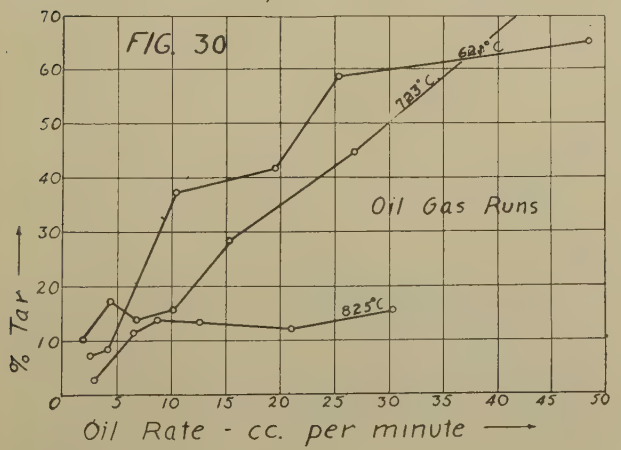


FIG. 30
621°C
723°C
825°C
Oil Gas Runs
% Tar
Oil Rate - cc. per minute

Fig. 30 shows clearly the effect of temperature on tar formation, and also the effect of increase of oil rate at constant temperature. The proportion of tar increases with increasing oil rate and most markedly so, at temperatures of 621° C. and 723° C. The largest proportion of these tars at moderate to high oil rates is undecomposed oil, as shown by distillation and treatment with concentrated sulfuric acid. This is also indicated by the fact that a temperature change from 621° C. to 723° C. produces no great difference in tar formation, and also by the fact of the very rapid increase in the percentage of tar with increasing oil rate.

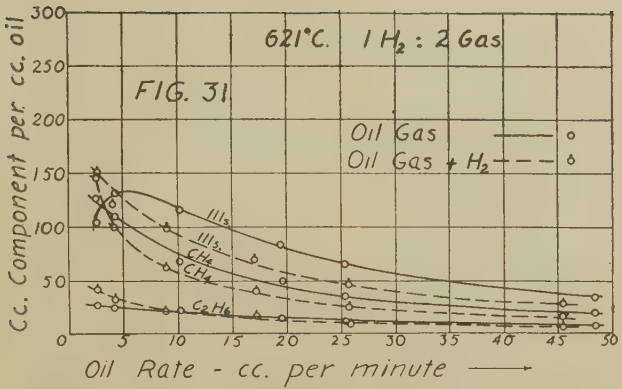
At 825° C. the proportion of tar does not increase greatly with increasing oil rate, indicating that these tars are largely composed of synthetic products, which is further substantiated by other physical characteristics, such as distinct aromatic odor and their reactions with concentrated sulfuric acid.

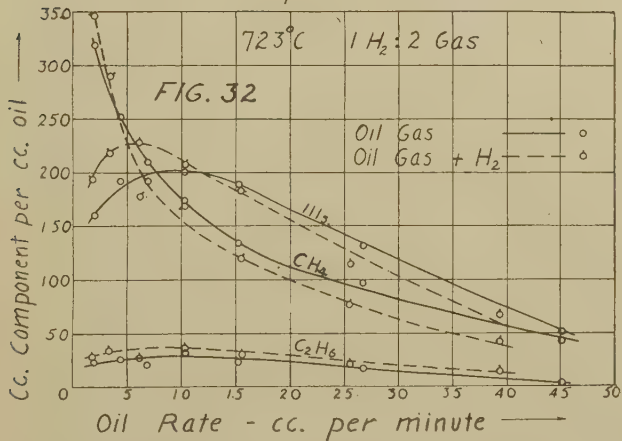
All the tars were strongly fluorescent.

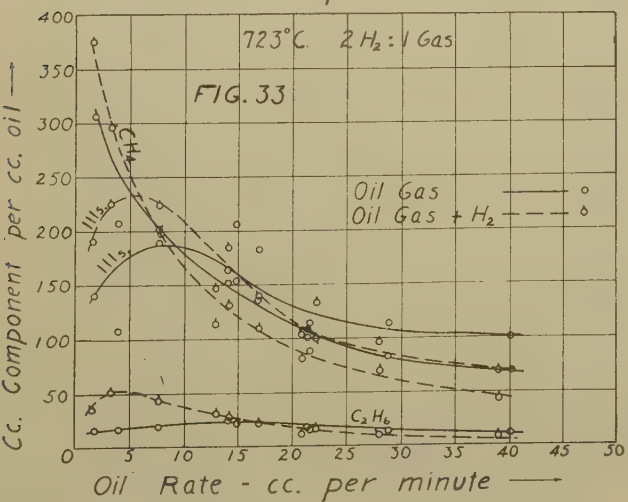
FORMATION OF ILLUMINANTS, METHANE, AND ETHANE, AND THE OBTAINING OF PARTICULAR END-PRODUCTS FROM A PARAFFIN HYDROCARBON OIL

In Figs. 31 to 35 the cc. of illuminants, methane and ethane formed from 1 cc. of oil are shown plotted against the oil rate at the temperatures and hydrogen-gas concentration ratios indicated. It can be seen from Fig. 31 that at 621° C., with the exception of the illuminants in the case of the straight oil-gas runs, the number of cc. of all these hydrocarbons formed from 1 cc. of oil increases with decreasing oil rate. There would be a limit to this, however, for, were the oil rate made low enough, a very extensive decomposition of the hydrocarbons would set in.

Fig. 31 shows that the illuminants are the most easily decomposed of the gaseous hydrocarbons. The curve for the illuminants in the straight oil-gas runs has a maximum due to the fact that though the longer time of contact of the oil vapors with the heated tube at low oil rates causes a more extensive formation of ethylene and other illuminants, an oil rate is reached where extensive decomposition of these hydrocarbons takes place, which more than overcomes the more rapid illuminants formation at low oil rates. Condensation and hydrogenation, which are more extensive at low oil rates, are important in this connection also.


621°C. 1 H_2 : 2 Gas
FIG. 31
Oil Gas
Oil Gas + H_2
111_3
111_{3-4}
CH_4
C_2H_6
Cc. Component per cc. oil
Oil Rate - cc. per minute


723°C 1 H_2 : 2 Gas
FIG. 32
Oil Gas
Oil Gas + H_2
111_3
CH_4
C_2H_6
Cc. Component per cc. oil
Oil Rate - cc. per minute


723°C. 2 H_2 : 1 Gas
FIG. 33
Oil Gas
Oil Gas + H_2
CH_4
111_{3-4}
111_3
C_2H_6
Cc. Component per cc. oil
Oil Rate - cc. per minute

No maximum is observed in the illuminants curve for the hydrogen runs, doubtless because the time of contact of the oil vapors with the heated tube is less at any particular oil rate than in the case of the oil-gas runs. The curve for the illuminants in the hydrogen-oil-gas runs, for this reason also, is always below that for the illuminants in the oil-gas runs, except at low oil rates.

Less methane is formed per cc. of oil in the hydrogen-oil-gas runs than in the straight oil-gas runs except at low oil rates. That the time of contact here is sufficient so that extensive hydrogenation takes place is clearly brought out from a consideration of Fig. 22 in connection with Fig. 31. At all oil rates the decreased time of contact of the gases with the heated furnace tube, on account of the absorption of hydrogen, results in a lower formation of methane.

The relationships for ethane are much the same as for methane, and for the same reasons.

Figs. 32 and 33 show the relationships between the hydrocarbons at 723° C. at hydrogen concentration ratios of $1H_2 : 2$ *Gas* and $2H_2 : 1$ *Gas*, respectively. More of each of the components is formed per cc. of oil at 723° C. than at 621° C. The maximum in the illuminants curve falls at a higher oil rate than at 621° C. as would be expected, since the higher temperature would cause a more rapid decomposition, condensation, and hydrogenation of the illuminants to take place. At 723° C. the maximum on the illuminants curve for the hydrogen runs can be seen clearly. It is interesting to note that this falls to the left of the maximum on the curve for the oil-gas runs. The decreased time of heating on account of the hydrogenation admixture is responsible for this.

The effect on the illuminants of increasing the concentration of hydrogen is clearly brought out in Figs. 32 and 33. The maximum on the curve for the illuminants in the hydrogen-oil-gas runs at the higher hydrogen concentration falls at a slightly lower oil rate than the maximum on the curve for the lower hydrogen concentration. The divergence between the illuminants curves for the oil-gas runs and the hydrogen-oil-gas runs is greater both at low and high oil rates at the higher hydrogen concentration than at the lower hydrogen concentration on the time of contact of the gases with the heated tube surfaces.

The relationships in the case of the methane and ethane are exceedingly interesting. The formation

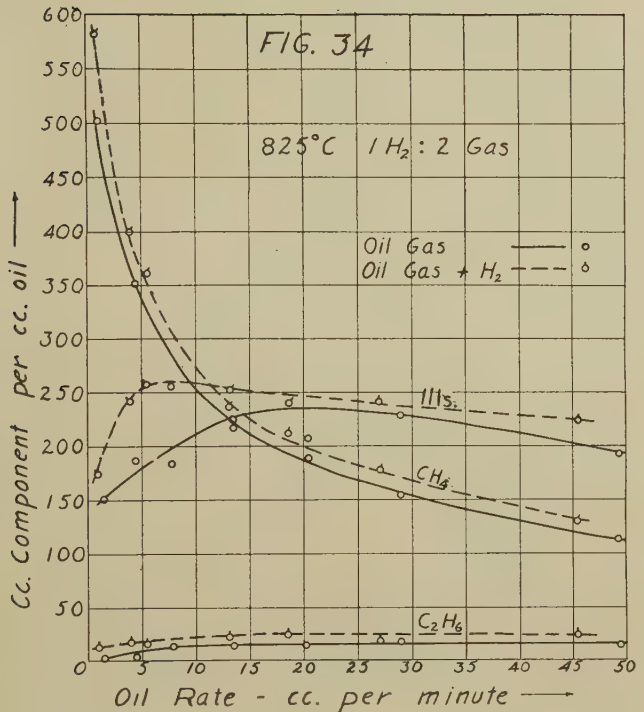
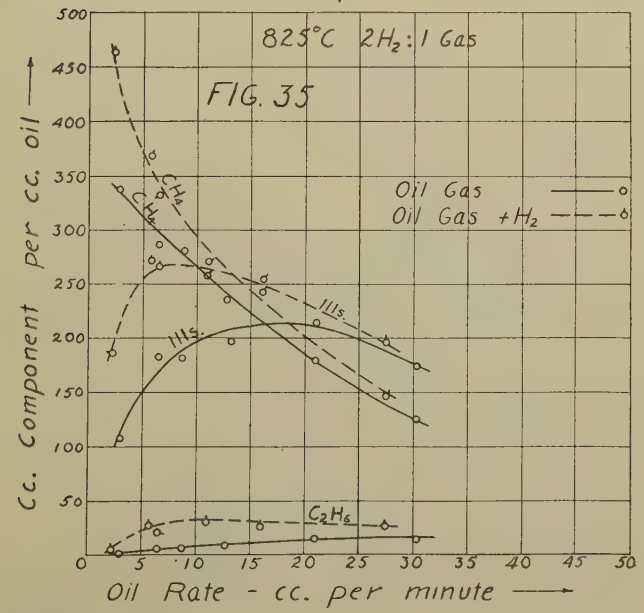


FIG. 34
825°C 1 H_2 : 2 Gas
Oil Gas
Oil Gas + H_2
CH_4
C_2H_6
Cc. Component per cc. oil
Oil Rate - cc. per minute


825°C 2H_2 : 1 Gas
FIG. 35
Oil Gas
Oil Gas + H_2
CH_4
C_2H_6
Cc. Component per cc. oil
Oil Rate - cc. per minute

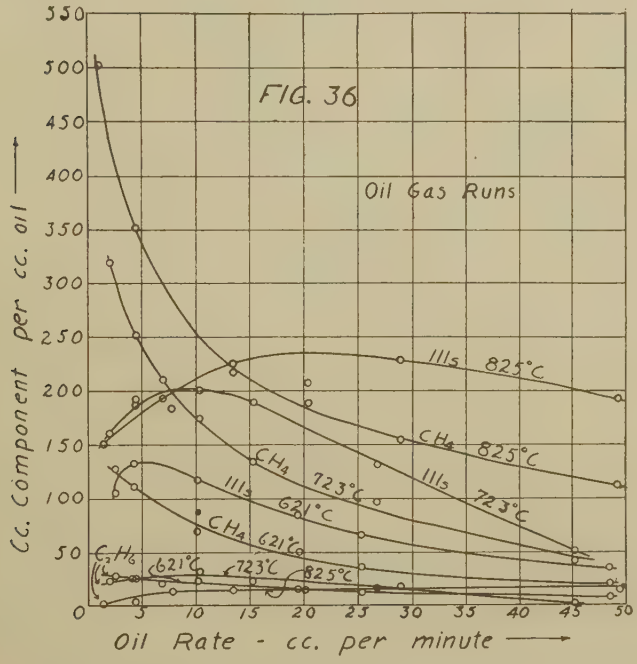
of methane is less in the hydrogen-oil-gas runs than in the oil-gas runs at moderate to high oil rates, due to the decreased time of contact of the gases with the heated surfaces, and this effect is more pronounced at the higher hydrogen concentrations, as would be expected. As the oil rate decreases the hydrogenation effect becomes important and the proportion of methane formed from 1 cc. of oil is greatest in the case of the hydrogen-oil-gas runs. The curve for methane in the hydrogen-oil-gas runs crosses the methane curve for the oil-gas runs. This crossing is at a higher oil rate with the higher hydrogen concentration, showing clearly the effect of the increase of concentration of hydrogen on the hydrogenation reactions. The formation of methane is slightly greater in the hydrogen-oil-gas runs than in the straight oil-gas runs when the hydrogen concentration ratio is *1 H_2 : 2 Gas*. This difference is slightly greater at low oil rates than at high oil rates.

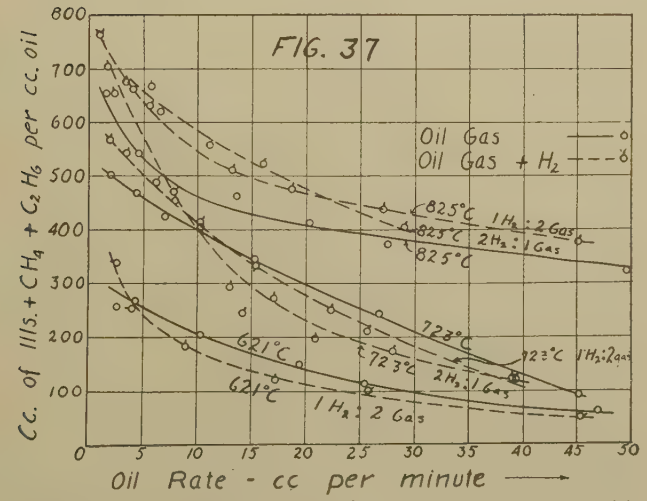
When the hydrogen concentration ratio is *2 H_2 : 1 Gas* the ethane formation per cc. of oil is less in the hydrogen-oil-gas runs than in the oil-gas runs at high oil rates. This is the effect of the decreased time of contact due to the admixture of a larger volume of hydrogen. But at low oil rates the formation of ethane is much greater in the hydrogen-oil-gas runs as can be seen in Fig. 33. The ethane curve has a maximum, too, which is interesting because it shows that at low oil rates the reactions of the hydrocarbon ethane itself have an important part to play.

Figs. 34 and 35 show the relationships between these hydrocarbons at 825° C. A much less pronounced decrease in the formation of illuminants with increasing oil rate is due to the fact that the temperature of 825° C. is sufficient to promote actively the formation of illuminants. The maxima on the illuminants curves for the oil-gas runs fall at the higher oil rates, as would be expected when the higher temperature is taken into consideration. The illuminants curves for the hydrogen-oil-gas runs are entirely above the illuminants curves for the oil-gas runs. This is again a result of the decreased time of heating when hydrogen is admixed. The effect is most marked when the higher concentration of hydrogen is used.

The curves for methane in the hydrogen-oil-gas runs fall above the curves for methane in the oil-gas runs at all oil rates at 825° C. This is due to two effects: *first*, the less extensive decomposition of the methane

into carbon and hydrogen due to the decreased time of heating in the hydrogen-oil-gas runs; *second*, the increased rate of hydrogenation reactions such as $C_2H_4 + 2H_2 \rightleftarrows 2CH_4$. The effect of hydrogen in





reversing the reaction $CH_4 \rightleftarrows C + 2H_2$ is probably not important, as has been brought out in the discussion of the methane equilibrium and the reactions of methane in the first part of this paper.

The effect of the greater concentration of hydrogen on methane production can be seen clearly by comparing Figs. 34 and 35. The divergence between the hydrogen-oil-gas and the oil-gas methane curves is greatest when the hydrogen concentration ratio is $2H_2 : 1\ Gas$, and this is practically true at low oil rates where hydrogenation reactions are most important.

More ethane is formed when hydrogen is mixed with the vapors of the oil than when it is not added. This is doubtless due to the combined influence of the hydrogen in diminishing the decomposition of the ethane and to its effect in hydrogenating the olefins. These effects are particularly marked when the concentration ratio is $2H_2 : 1\ Gas$.

It may have been noticed that the curves for the oil-gas runs made at the same temperature do not coincide exactly, since the carbon tube used carbonizes somewhat and becomes of smaller internal diameter, thus decreasing the time of contact of the gas with the tube and consequently altering the composition somewhat.

The effect of temperature on the hydrocarbon products of decomposition of an oil can be seen very clearly from Fig. 36. Within the temperature range studied, the cc. of illuminants per cc. of oil increases with temperature, with one exception. At low oil rates there are more illuminants formed at 723° C. than at 825° C. The effect of the higher temperature in increasing the speed of the reactions which decompose ethylene more than overcomes the effect of the higher temperatures in promoting the decomposition of the long chain olefins to ethylene and propylene.

It is interesting to note the position of the maxima of the curves for the illuminants at the several temperatures. These maxima indicate where the balance between the reactions of formation and the reactions of decomposition falls.

Within the temperature range studied, the formation of methane is greater the higher the temperature. At low oil rates the difference in the methane produced by a 100°-temperature rise is greater in the range from 621 to 723° C. than from 723 to 825° C., since at low oil rates 723° C. is a sufficiently high temperature to break down the original oil extensively. The methane increase between 723 and 825° C. is largely due to the decomposition and hydrogenation of

olefins $C_2H_4 \longrightarrow C + CH_4$ and $C_2H_4 + 2H_2 \rightleftharpoons 2CH_4$, as can be seen from a consideration of the illuminants curve for 825° C.

At high oil rates a temperature of 825° C. is necessary to form methane largely, as can be seen from the position of the curve for methane at 621, 723 and 825° C.

The formation of ethane per cc. of oil is not large at any temperature studied, as shown in Fig. 36. The primary decomposition of the oil therefore involves chiefly a splitting off of methane rather than ethane or higher paraffin. The decomposition and dissociation of ethane are clearly shown by the falling off of the ethane curve as the oil rate decreases at a temperature of 825° C. On the other hand, a temperature of 825° C. is necessary to cause an extensive formation of methane and ethane per cc. of oil at high oil rates.

TOTAL HYDROCARBONS OBTAINABLE FROM THE OIL

The greater the proportion of the carbon of the oil which can be obtained in gaseous form the better the utilization of the oil for gas-making purposes.

Fig. 37 shows the *Total cc. of Illuminants + methane + ethane* obtainable from 1 cc. of oil under the varying conditions. At 621° C. more hydrocarbons are obtained per cc. of oil in the oil-gas runs than in the hydrogen-oil-gas runs, except at low oil rates where hydrogenation reactions become important. This is due to the lower time of contact of the oil vapors with the furnace tube in the case of the hydrogen-oil-gas runs. The same relations hold at 723° C. except that the hydrogen-oil-gas curves cross the oil-gas curve at a higher oil rate because of the greater effect of the higher temperature in hastening the hydrogenation reactions. The effect of the higher concentration of hydrogen is clearly shown. At 825° C. the hydrocarbons formed per cc. of oil are of greater volume in the hydrogen-oil-gas runs at all oil rates studied. The higher temperature promotes hydrogenation reactions at all oil rates. The effect of the greater concentration of hydrogen can be seen.

It is interesting to note that the slope of the curve for the hydrogen-oil-gas runs at 723° C. is much steeper than the slope of these curves at 825° C. at low oil rates, doubtless because at 825° C., and low oil rates, dehydrogenation reactions and reactions of decomposition of the hydrocarbons become of importance.

1—A critical review of the most important work on hydrocarbon decomposition and the influence of hydrogen on the reactions involved has been given. This has concerned itself with: *first*, the hydrocarbons of high molecular weight; *second*, the products of the primary decomposition; and *third*, the reactions of the simpler hydrocarbons. Summaries have been included which state concisely the probable course of the reactions of dissociation, decomposition, and condensation involved.

2—The subject of the mechanism of heat transfer in gas machines has been discussed.

3—Difficulties in the measurement of the true temperature of a gas have been pointed out.

4—In the experimental work a paraffin oil was thermally decomposed alone and in hydrogen at temperatures of 621, 723 and 825° C. Concentrations of hydrogen approximating $1H_2$: 2 *Oil Gas* and $2H_2$: 1 *Oil Gas* were those studied. It has been shown what results may be expected in the decomposition of a hydrocarbon oil when temperature, rate of oil feed, and concentration of admixed hydrogen are carefully controlled.

5—The relationship between the rate of oil feed and the rate of gas generation has been brought out.

6—The proportions of illuminants, saturated hydrocarbons, and hydrogen resulting at varying rates of oil feed, and at temperatures of 621, 723 and 825° C. have been shown graphically and discussed.

7—The effects of hydrogen on the reactions which give rise to saturated hydrocarbons and illuminants have been shown graphically and discussed at some length. Besides its effect in hydrogenating olefins and other hydrocarbons, the hydrogen, since its addition causes an increase in the total volume of the gas passing through the heated zone of the furnace in a given time, decreases the time of contact of the gases with the heated walls of the resistor tube. The effects of this are discussed in connection with the curves showing the relationships between the components of the gas when the oil is cracked in hydrogen.

8—The mean molecular weight of the olefins in a series of gases made at 825° C. has been determined, and also the proportion of aromatic hydrocarbons in these gases.

9—The formation of tar was studied at the various oil rates, temperatures and concentrations of hydrogen.

10—Curves showing the number of cc. of illuminants, ethane, and methane obtainable from 1 cc. of oil have been shown.

11—In general the manner of decomposition of a paraffin hydrocarbon oil has been mapped out over a considerable range of temperature, rate of oil feed, and concentration of hydrogen.

12—The results recorded in this paper may serve as a guide to the obtaining of more desirable results in commercial operations involving the decomposition of oil for gas-making purposes.

CONCLUSIONS

In addition to showing the proportions of products which are obtainable under a variety of conditions, which relationships have been fully set forth in the figures shown and which it is impossible to briefly summarize, it has been concluded as a result of this investigation:

I—That the importance of radiation insofar as it is concerned in the furnishing of the energy for the production of hydrocarbon reactions has been overestimated.

II—That effects often ascribed to catalysis are in reality due to effective heat transfer by conduction and convection from the large heated surfaces exposed to the gases.

III—That the equilibrium condition is not attained in a hydrocarbon system when an oil is decomposed by heat under conditions analogous to those of carbureted water-gas manufacture.

IV—That the course of the changes involved in the breaking down of a hydrocarbon oil may be roughly traced.

V—That hydrogen is produced from an oil even when the cracking takes place in hydrogen.

VI—That considerable absorptions of hydrogen take place when an oil is cracked in an atmosphere of hydrogen, and this absorption is greater the higher the concentration of hydrogen, the higher the temperature (within the range studied), and the lower the oil rate.

VII—That propylene and higher olefins constitute approximately one-third by volume of the illuminants of the gas.

VIII—That the proportion of tar increases with decrease in temperature, and with increasing oil rate, particularly at the lower temperatures.

IX—That no marked and consistent difference in the amount of tar formed when an oil is decomposed alone or in hydrogen at temperatures of 723° C. or below is noticeable. At 825° C. less tar is formed when the oil is cracked in hydrogen. The tars formed below 723° C. are in large part unchanged or partly changed oil, whereas those tars formed above 800° C. are essentially composed of synthetic products.

X—That the reactions which result in decreasing the proportion of illuminants are the most rapid.

XI—That the presence of hydrogen during the decomposition of an oil has the effect of increasing largely the proportion of the carbon of the oil appearing as hydrocarbons in the gas.

XII—That within the temperature range studied the volume of illuminants produced per volume of oil increases with the temperature with one slight exception. The formation of methane is greater the higher the temperature. The formation of ethane is not large at any temperature and therefore the primary decomposition of an oil involves chiefly a splitting off of methane rather than ethane or higher homologs.

XIII—That a temperature of 823° C. is desirable in decomposing an oil provided that too great opportunity for extensive secondary and tertiary change is not given.

XIV—That with correct design of apparatus, and proper adjustment of temperature, rate of oil feed, and concentration of hydrogen it is possible to obtain gases of widely varying compositions.

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VITA

Eugene Hendricks Leslie was born at Ottawa, Illinois, August 28, 1892.

He was graduated from the Ottawa High School in June, 1909, and in the Fall of that year he entered the University of Illinois. From this institution he was graduated in June of the year 1913 with the degree of Bachelor of Science in Chemical Engineering.

In September, 1913, he entered Columbia University where he has been in continuous residence to this date. During this time he has been engaged in graduate study and research work and has held an assistantship in the Department of Chemistry. He has also been an officer of instruction in the intervening summer sessions at Columbia, and in Extension Teaching.